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November 2, 2001

Mr. Tien Q. Duong  
5G-030, EE-32  
Forrestal Building  
U.S. Department of Energy  
Washington D.C. 20585

Dear Tien:

Here is the fourth-quarter FY 2001 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior (ETR) Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATT.html>.

Sincerely,

Frank McLarnon  
Manager  
BATT Program

cc:	R. Sutula	DOE/OAAT
	K. Heitner	DOE/OAAT
	R. Kirk	DOE/OAAT
	V. Battaglia	ANL
	J. Krupa	DOE-Oakland

LBID-2395

# **BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)**

## **QUARTERLY REPORT**

## **TABLE OF CONTENTS**

Task Status and Progress Toward Milestones Reports  
by Research Area

Proposals Under Review

Calendar of Meetings

## **BATT TASK 1 CELL DEVELOPMENT**

### **TASK STATUS REPORT**

**PI, INSTITUTION:** K. Striebel, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Development - Cell Fabrication and Testing

**SYSTEMS:** Low-Cost Li-Ion, High-Power Li-Ion

**BARRIER:** Inconsistent evaluation of the merits of candidate novel materials.

**OBJECTIVES:** The primary objective is to establish a test vehicle for the evaluation of new materials for high-power and low-cost Li-ion cells.

**APPROACH:** The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. This task is a collaborative effort, which includes the development of an appropriate test vehicle (cell geometry), electrochemical cycling, and cell disassembly. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell with appropriate ratios of components (*i.e.*, active materials/electrolyte volume) and tested with a consistent protocol to determine capacity, energy, power, and lifetime characteristics. Components are then delivered to the PI's involved with BATT Program diagnostics. Fabrication and testing of the third baseline cell, *i.e.*, Li metal/polymer/V<sub>6</sub>O<sub>13</sub>, will be carried out in the Electrolyte Task.

**STATUS OCT. 1, 2000:** This is a new project with the start date of October 1, 2000.

**STATUS SEPT. 30, 2001:**

- Equipment has been assembled and a process has been developed for the preparation PVdF-bonded composite electrodes and the assembly of laminated-foil pouch cells (12 cm<sup>2</sup>) with separator and liquid electrolyte
- A test protocol was developed, including C/2 100% DOD cycling with periodic power characterization, and used to compare power fade for gel technologies from Doo Youn Corp., UltraLife, and Toshiba
- Gen 2 chemistry pouch cells with both Quallion and LBNL-made cathodes cycled 160 times with <5% capacity fade, providing verification of the pouch cell process
- The high-power baseline cell chemistry has been benchmarked in constant-current testing. Cells have been received from Hydro Quebec for the benchmarking of the high-energy baseline cell against current USABC goals.

**RELEVANT USABC GOALS:** 10 year life, <20% capacity fade over a 10-year period.

**MILESTONE:** Baseline cell fabrication techniques and test protocols have been established.

## PROGRESS TOWARD MILESTONES

### Accomplishments toward milestone over last quarter:

A complete pouch cell fabrication and testing lab has been set up. Capabilities include the casting of anodes and cathodes in the desired thickness onto Cu or Al current collector foils. These electrodes can then be densified in a roll-press, as desired. Al (+) or Ni (-) pre-sealable tabs are attached to the current collectors with an ultrasonic welder. The electrode assemblies are dried in a vacuum antechamber and transferred to an Ar-filled glovebox. Cells are assembled with the desired separator, sealed into pouches and filled with a metered amount of electrolyte, with or without thermally cross-linkable gelling polymer components. A Sn micro-wire reference electrode can be added to the pouch for aid in identifying the source of any impedance rise in the cells. Cells are removed from the glovebox and tested with a standard protocol in the room or in a temperature-controlled (-40 to +60°C) environmental chamber. Electrode and pouch cell construction details, as well as physical tests on the active materials and electrochemical tests on the cells or components are logged into an Access database. Portions of this database are available on the web. At present, the web-enabled portion is in the prototype stage and the URL is not available for public access. In the near future, parties interested in viewing the BATT data may apply for a password and instructions.

The power fade and cycle capability of commercially available, cell-phone size, LiCoO<sub>2</sub>/graphite cells with gel or liquid electrolyte from Toshiba, Doo Youn (Korea), UltraLife and Quallion Corp, were studied during the development of testing protocols. All types held more than 80% original capacity during C/2 100% DOD cycling for at least 400 cycles. The ASI measured at 80 cycle intervals increased moderately (30 – 60%) for all of the cells tested, except for the Toshiba cell. This cell showed remarkable power retention out to 400 cycles. A manuscript describing these studies is in preparation.

Pouch cell preparation techniques were verified concurrent with the establishment of benchmark performance for the high-power baseline chemistry: Gen 2 as defined in the ATD Program. The performance of pouch cells prepared from Quallion-made Gen 2 electrodes compared well with that of LBNL-made electrodes with the same composition. The performance of the LBNL-pouch cells compares extremely well with the behavior of 0.1 and 1Ah Gen cells, received from Quallion. These studies have been extended to characterize the behavior of this chemistry during high and low temperature cycling as well as 80% DOD cycling. A small Gen 2 cell cycled at 100% DOD for >400 cycles showed a power fade on the order of 45%. The capacity fade recorded at C/2 was caused directly by this impedance rise because the cell showed essentially the same C/25 capacity as the fresh cell. Some of these results were presented at the ECS meeting in San Francisco. Two manuscripts are in preparation.

- **Further plans to meet or exceed milestones:**

The characterization of the baseline high-energy cell is now in progress. Ten cells with LiFePO<sub>4</sub>, graphite electrodes and LiBF<sub>4</sub>-containing gel electrolyte were received at the end of the FY from Hydro-Québec. Prior to this, small samples of LiFePO<sub>4</sub> powders and thin electrodes were received for preliminary studies in button cells as reported in Task 4. A few samples of Li<sub>x</sub>Al<sub>0.25</sub>Mn<sub>1.75</sub>O<sub>3.98</sub>S<sub>0.02</sub> were obtained from Task 4. Benchmarking of this material in pouch cell studies will be carried out next quarter and compared with data already available for Li<sub>1+y</sub>Mn<sub>2-y</sub>O<sub>4</sub> (Merck) cells.

- **Reason for changes from original milestones:** N/A

## TASK STATUS REPORT

**PI, INSTITUTION:** T.J. Richardson, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cell Development - Materials Characterization Using X-Ray Diffraction and Chemical Analysis

**SYSTEMS:** Li/Polymer, Low-Cost Li-Ion

**BARRIER:** Short lithium battery lifetimes.

**OBJECTIVES:** Accelerate evaluation of electrode materials by structural characterization of active components as received (or synthesized), following cell disassembly, and *in situ* during cycling. Assist in electrode materials development.

**APPROACH:** Analyze cycled electrodes taken from baseline BATT Program cells, seeking deleterious phase transformations in the bulk of the active material and accumulated inactive decomposition products.

**STATUS OCT. 1, 2000:** This is a new task as of Oct. 1, 2000.

**STATUS SEPT. 30, 2001:** Establish active material compositions of cycled and uncycled electrodes from Cell Development and Cathode investigators (Striebel and Doeff). Correlate phase transformations and accumulation of decomposition products with cell cycling performance.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONES:** Determine phase compositions in cycled electrode materials by the planned date of June 1, 2001.

## PROGRESS TOWARD MILESTONES

### Accomplishments toward milestone over last quarter

Electrodes taken from cycled commercial Li-ion batteries supplied by K. Striebel were examined by X-Ray diffraction. No new phases were found in these electrodes.  $\text{LiCoO}_2$  electrodes, supplied by Quallion, were examined following mild overcharging excursions. XRD patterns of these electrodes (Fig. 1) show gradual conversion to a second phase, which is tentatively identified as  $\text{Co}_3\text{O}_4$ .

A study of the effects of overcharge and overdischarge on  $\text{LiFePO}_4$  electrodes was undertaken using x-ray diffraction, infrared spectroscopy, and cyclic voltammetry. No new phases were detected in these electrodes by XRD or by FTIR. Figure 2 shows the FTIR spectra of  $\text{LiFePO}_4$ ,  $\text{FePO}_4$  prepared by chemical oxidation with  $\text{NO}_2\text{PF}_6$  in  $\text{CH}_3\text{CN}$ , and an overcharged  $\text{LiFePO}_4$  electrode. Reaction of  $\text{FePO}_4$  with additional  $\text{NO}_2\text{PF}_6$  resulted in dissolution of much of the solid. Dissolution appears to be the mechanism for capacity fading caused by overcharging. Sequential cyclic voltammograms (0.050 mV/s) between 2.5 and 5.75 V (Fig. 3a) show progressive loss of capacity and decreased reversibility, but no new features. Overdischarging to 1.0 V (Fig. 3b) results in very slow capacity loss with no change in reversibility, suggesting reversible formation of an inactive surface layer.

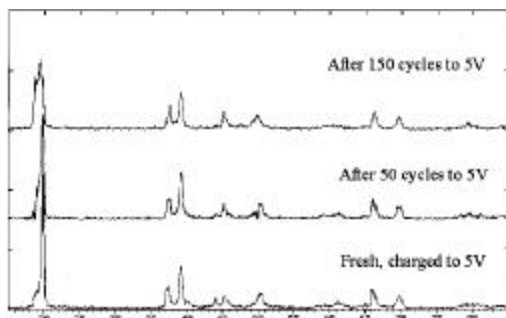


Figure 1

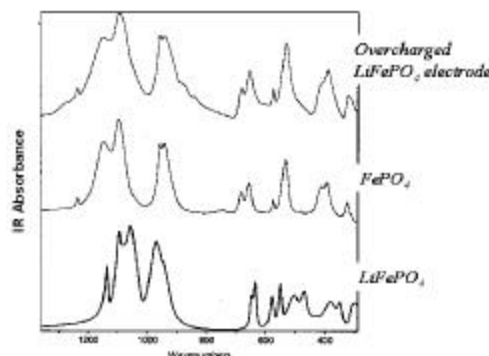


Figure 2

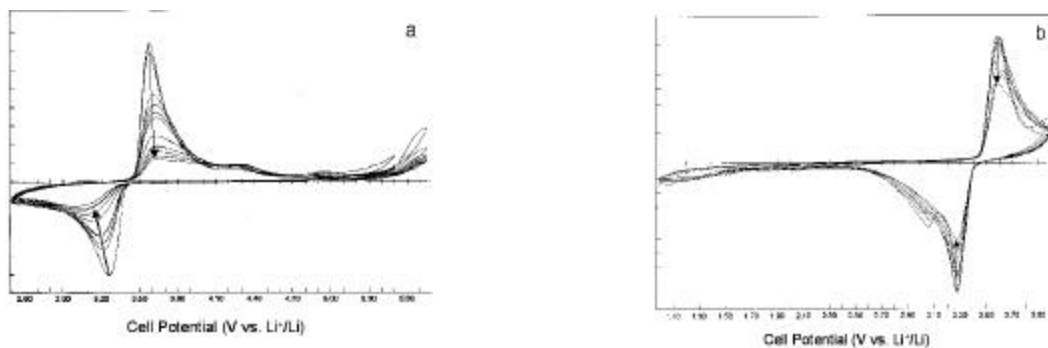


Figure 3

- **Further plans to meet or exceed milestones:** Additional potentially useful electrode materials will be synthesized and evaluated. Milestone was achieved.
- **Reason for changes from original milestones:** N/A

## **TASK STATUS REPORT**

**PI, INSTITUTION:** K. Zaghib, Hydro-Québec Research Institute

**TASK TITLE - PROJECT:** Electrolytes - Research on Lithium-Ion Polymer Batteries Utilizing Low Cost Materials

**SYSTEMS:** Low-cost lithium-ion

**BARRIER:** High cost of Li-ion batteries

**OBJECTIVES:** (a) To fabricate Li-ion polymer cells (4 cm<sup>2</sup> area) using cell chemistries proposed by DOE. Cells (50% of the total cells) will be sent to LBNL for testing. (b) To investigate interfacial phenomena at the anode/separator and cathode/separator in Li-ion polymer cells. (c) To determine the cycle life of Li-ion polymer cells at different temperatures (55°C to 0°C) and self-discharge rates. (d) To synthesize low-cost graphite anode and LiFePO<sub>4</sub> cathode material for Li-ion polymer cells.

**APPROACH:** Our approach is to synthesize and coat electrodes (anode and cathode) with low-cost materials, and use these materials to assemble a flat cells. More work will focus on gel polymers. The task includes the study of pressure effects and interfacial phenomena at the polymer/electrode interface.

**STATUS OCTOBER 1, 2000:** This is a new task as of May 2001.

**STATUS SEPTEMBER 30, 2001:** We expect to fabricate and send 10 cells to LBNL for evaluation. Cells will also be tested at HQ to determine the effects of pressure.

**RELEVANT USABC GOALS:** 10 year life, < 20% capacity fade over a 10-year period.

**MILESTONES:** Ten cells will be provided to LBNL for evaluation each quarter following the start of the contract.

## PROGRESS TOWARD MILESTONES

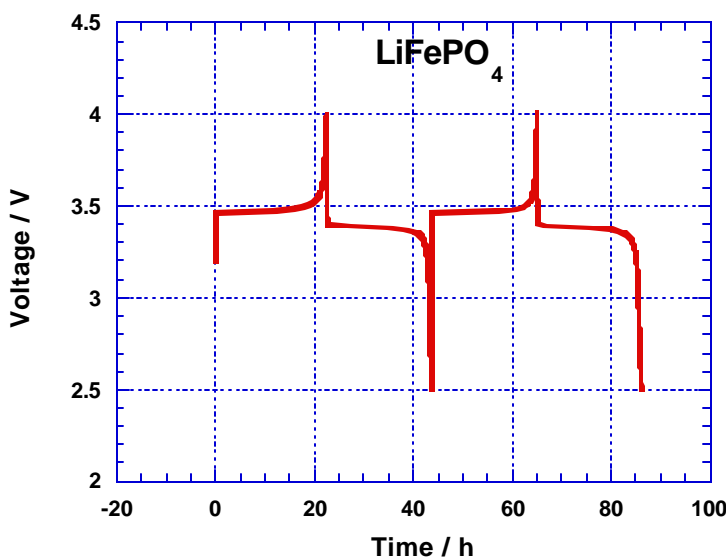
- **Accomplishments toward milestone over last quarter**

We have completed physicochemical and electrochemical characterization of  $\text{LiFePO}_4$  synthesized at the University of Montreal (UM). The compositions of positive and negative electrodes were optimized (i.e., proportion of binders, conductor agent and active materials) and coated on aluminum and copper current collectors, respectively, to obtain the desired capacity balance (10 to 20% excess of anode).

Several 5-g batches of cross-linkable HQ polymers based on polyether were prepared: the first one by an over coating Celgard membrane ( $8\mu\text{m}$ ), and the second one is a freestanding HQ polymer-type film with  $20\mu\text{m}$  thickness.

$\text{LiFePO}_4$  (UM) low-cost cathode material, surface treated with carbon with less than 1% by weight, was evaluated at  $25^\circ\text{C}$  in EC-DEC –1M  $\text{LiClO}_4$ . The result showed highly reversible capacity at the C/24 rate with 160 mAh/g, 10 mAh/g lower than the theoretical capacity.

Several Li-ion gel-type cells were prepared and ten cells were sent to LBNL for evaluation. In addition, positive and negative electrodes containing  $\text{LiFePO}_4$  and natural graphite, respectively, were sent to LBNL.



- **Further plans to meet or exceed milestones:**

We have also begun a collaboration with LTEE (Shawinigan) to produce gel electrolyte. We will continue working with LBNL to transfer technology to assemble gel cells (coin type or flat cells).

- **Reason for changes from original milestones:** N/A



## BATT TASK 2 ANODES

### TASK STATUS REPORT

**PI, INSTITUTION:** K. Kinoshita, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Anodes - Carbon Materials

**SYSTEMS:** Low-Cost Li-Ion

**BARRIER:** High Cost of Li-Ion Batteries

**OBJECTIVES:** The primary objective is to identify a low-cost carbon (<\$10/kg) for negative electrodes in Li-ion batteries for electric and hybrid vehicles.

**APPROACH:** We have continued our collaboration with industry (mainly Hydro-Québec) to develop low-cost carbons for Li-ion batteries. Our role will be to utilize the analytical and spectroscopic facilities at LBNL to characterize the properties of the carbons. Techniques such as high-resolution electron microscopy, scanning electron microscopy, Raman spectroscopy, X-ray diffraction analysis and thermal analysis will be used to determine the physicochemical properties of carbon. Electrochemical studies to determine the reversible capacity and irreversible capacity loss of the carbons will be conducted in laboratory-scale cells.

**STATUS OCT. 1, 2000:** Our results suggest that there is a strong correlation between the irreversible capacity loss and the relative fraction of edge sites associated with the graphitized carbon sample. Within the range of graphite particle sizes considered in the study, there is no significant correlation between reversible capacity and the structural parameters associated with the crystallite size (*i.e.*,  $L_c$ ,  $L_a$ ). These results were obtained at reasonably low charge/discharge rates. We plan to examine these effects at higher rates to determine the influence of particle size on the initial reversible capacity. The correlation with cycle life was not investigated because we are not confident that the cells available (in-house) are adequate for cycle testing. This study was conducted in collaboration with Hydro-Québec.

**STATUS SEPT. 30, 2001:** A chemical procedure to purify natural graphite that is lower cost than thermal purification processes was developed in collaboration with Hydro-Québec. Optimizing the chemical composition to produce purified graphite has not been completed. Thermal analysis involving oxidation of the NG samples clearly showed that the initial oxidation temperature was considerably lower when impurities were present.

**RELEVANT USABC GOALS:** Develop low-cost carbon to meet the cost target for battery of <\$150/kWh.

**MILESTONES:** Complete analysis of particle-size effect on high-rate charge/discharge of flake graphite in liquid electrolyte. (03/01)

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Collaboration between LBNL and Hydro-Québec is focused on identifying a viable chemical route to produce low-cost graphite (<\$5/pound) for negative electrodes in Li-ion batteries. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed at a heating rate of 10°C/min in air to screen the graphite samples. The TGA/DTA studies provide a rapid and sensitive measure of the level of impurities because many of the impurities respond as oxidation catalysts that lower the onset temperature for oxidation.

The oxidation behaviors of several graphite samples (all have 20 µm average particle size) were measured. The oxidation of unpurified graphite (HQ16) occurs at a lower temperature, as expected. The purified samples from Japan (NG20) and Hydro-Québec (HQ22) show similar oxidation behavior. On the other hand, HQ37, purified with HF in Brazil (used in alkaline batteries), oxidizes at much higher temperatures. There is no significant difference in the purity of the purified samples (all 99.9%+). However the types of impurities that remain may be different, depending on the chemical purification process. Experiments are underway to determine the elemental composition of these samples and to examine their morphology.

- **Further plans to meet or exceed milestones**

Milestone has been completed and reported in the first quarterly report for Fiscal Year 2001. Focus of this task will shift to development of low-cost graphites for Li-ion batteries. The effort will be conducted in collaboration with Hydro-Québec. A common sample of natural graphite (98%purity) from Brazil will be purified by chemical (at HQ) and thermal (at LBNL) treatments. We are interested in comparing the impurity levels, types of impurities and electrochemical performance of the purified NG obtained by the two treatments.

- **Reason for changes from original milestones:** N/A

## TASK STATUS REPORT

**PI, INSTITUTION:** G.A. Nazri and M.D. Curtis, University of Michigan

**TASK TITLE – PROJECT:** Anodes - Optimization of Anodes for Li-Ion Batteries

**SYSTEMS:** Low-Cost Li-Ion

**BARRIER:** Safety, irreversible capacity loss, and self-discharge.

**OBJECTIVES:** The primary objective is to improve the overall safety, cycle life, and shelf life of the Li-ion battery, through development of a low-cost surface treatment process to stabilize the anode/electrolyte interface and reduce cell impedance.

**APPROACH:** Our approach is to stabilize the anode/electrolyte interface to prevent self-discharge, electrolyte decomposition, and improve safety aspects of the Li-ion battery. We are engineering an artificial SEI layer on anodic materials to provide superior thermal and chemical stability, as well as a high Li-ion conductivity for application in high-power Li-ion batteries. The work is focused on the ATD Program Gen 2 chemistry, as well as the application of EC-EMC electrolytes for sub-ambient-temperature performance.

**STATUS OCT. 1, 2000:** We developed a Li-phosphonate based polymer stable in the operational voltage range of carbonaceous anodes with the added benefit of fire-retardant properties. We also developed a unique *in situ* technique to explore the reactivity of anode/electrolyte interfaces.

**STATUS SEPT 30, 2001:** New electrically conductive polymers have been prepared for use as simultaneous binder/artificial SEI. The polymers feature a conjugated backbone and pendant groups that are anticipated to enhance Li ion conductivity, decrease the reactivity of the carbon/electrolyte interface, and decrease the cell impedance. Further, high volumetric energy density compounds have been incorporated in the graphitic anodes to improve their volumetric energy density.

**RELEVANT USABC GOALS:** Improved safety of Li-ion batteries, long cycle and shelf life, compatibility for high-power batteries.

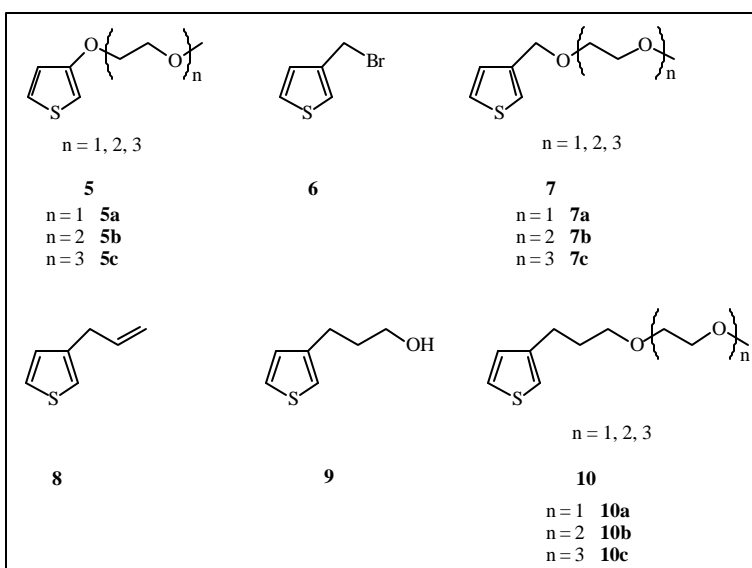
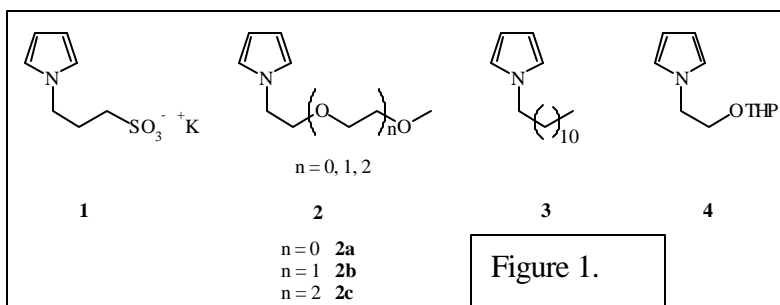
**MILESTONES:** Milestones to synthesize and coat carbonaceous materials for anodes have been realized. Characterization of the materials is mostly complete, and the construction of electrochemical cells incorporating the new materials and testing their performances are in progress. Or new milestones are the completion of the physical, chemical, and electrochemical characterization of the new materials, and obtaining performance data of cells constructed with the new materials. It is expected that these tests will be completed by the end of our current grant period.

## PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone over last quarter**

Recently, the bulk of our effort has been concentrated on monomer synthesis. Two classes of monomers have been produced, those based on pyrrole (Fig. 1) and those based on thiophene (Fig. 2). Both monomer sets contain materials with side chains designed to facilitate the conduction of lithium ions. In addition, the members of each group can be polymerized fairly easily either chemically or electrochemically. Electrochemical methods have been employed which involve deposition of a doped polymer film onto a positively charged electrode. In order to obtain large quantities of these materials, chemical polymerization using ferric chloride has also been undertaken.

We have also incorporated Si nanoparticles in the graphitic anodes to enhance the volumetric energy density of the anode. Optimization of the composite anode is in progress.



**Figure 2.** Thiophene monomers

- Further plans to meet or exceed milestones**

Most of our future work will consist of optimization of composite anodes to achieve higher volumetric energy density and characterization of materials already produced. For the characterization of materials already synthesized, conductivity/impedance measurements are completed.

Finally, the battery electrodes are constructed by applying these materials onto graphite. Through the results of the conductivity/impedance measurements and data obtained from cell cycling trials, the optimum polymer composition and overall composition of the composite anode will be achieved.

- Reason for changes from original milestones:**

We have added a task to improve the volumetric energy density of the anode, as indicated in our recent AOP.

## TASK STATUS REPORT

**PI, INSTITUTION:** M. Thackeray, Argonne National Laboratory

**TASK TITLE:** Anodes - Non-Carbonaceous Materials

**SYSTEMS:** Low-Cost Battery

**BARRIER:** Cost and safety limitations of Li-ion batteries.

**OBJECTIVES:** To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

**APPROACH:** Our approach is to search for, characterize, and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and that provide capacities  $>400$  mAh/g and  $>1000$  mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The task entails the synthesis and electrochemical evaluation of the intermetallic electrodes and their structural characterization by X-ray diffraction and spectroscopy. The reactivity of the intermetallic electrodes with the electrolyte will be determined by calorimetric techniques.

**STATUS OCT. 1, 2000:** We identified intermetallic compounds with nickel-arsenide and zinc-blende structure types for possible exploitation as anodes for Li batteries.  $\text{Cu}_6\text{Sn}_5$  and  $\text{InSb}$  were identified as test cases for the preliminary investigations of these types of materials, respectively; they yield reversible capacities of 200 mAh/g and  $>1000$  mAh/ml for 10-15 cycles. These novel materials have exciting prospects for further development and improvement in performance.

**STATUS SEPT. 30, 2001:** Improvements in electrochemical performance from either new or modified intermetallic electrode compositions based on tin and antimony compounds will have been achieved. We expect to have improved the cycling stability of these materials with reversible capacities of 250 mAh/g and  $>1000$  mAh/ml for 40 cycles. We will have obtained preliminary data regarding the thermal stability of the intermetallic electrodes with respect to organic-based electrolytes. We will also have gathered a more-detailed understanding of the behavior of NiAs and zinc-blende electrodes in electrochemical cells.

**RELEVANT USABC GOALS:** 10-year life,  $<20\%$  fade over a 10-year period.

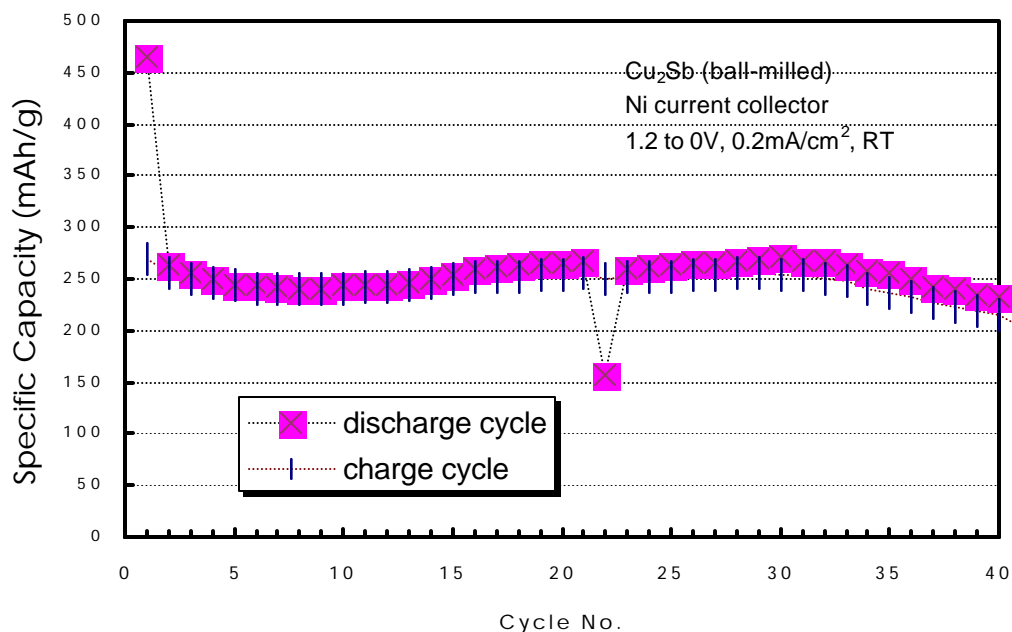
**MILESTONES:** The primary milestone will be to increase the reversible electrochemical capacity of tin- and antimony-based electrodes from 200 to 250 mAh/g for 20 cycles by the end of April 2001, by which time preliminary calorimetric data will also have been gathered. A target of reaching a capacity of 250 mAh/g for 40 cycles by end of September 2001 has been set, by which time a greater insight of the electrochemical mechanisms of tin- and antimony-based systems will also have been gathered to enable the identification of cost-effective intermetallic electrode structures.

## PROGRESS TOWARD MILESTONES

### Accomplishments toward milestone over last quarter

Work over the past six months has focused on studying the properties of substituted  $\text{Cu}_{6-x}\text{M}_x\text{Sn}_{5-x}\text{N}_x$  electrodes, where M is a transition metal and N is a main group metal and  $\text{Cu}_2\text{Sb}$  electrodes. The materials were synthesized and evaluated in lithium cells. Early results show that these substituted electrodes deliver a slightly lower capacity ( $\sim 150$  mAh/g) than  $\text{Cu}_6\text{Sn}_5$  electrodes, but show excellent cycling stability in the tests that have been conducted thus far (14 cycles). In particular, we have continued examining the role of the current collector on the electrochemical performance of the system. For Cu-backed electrodes, the transformation of  $\text{Li}_2\text{CuSn}$  to  $\text{Cu}_6\text{Sn}_5$  occurs at approximately 0.84V, whereas Ni-backed electrodes appear to suppress this transformation. In addition, we have initiated an investigation of the solubility of aluminum in the copper-tin system to increase the capacity and reduce the mass of the electrode. Preliminary data have shown that solubility is limited without counter-doping on the transition metal site. With Zn counter doping (maintaining the total electron count), up to 20% of the tin can be substituted for aluminum. Work continues on this system.

We expanded our efforts on copper-based electrodes to include the copper-antimony system that forms a ternary intermediate compound with lithium,  $\text{Li}_2\text{CuSb}$ , which is isostructural with  $\text{Li}_2\text{CuSn}$ . In addition, we investigated the effect of synthesis temperature on the performance of the intermetallic electrode. Ball-milled samples or those annealed above  $400^\circ\text{C}$  typically provide an average 250 mAh/g for 40 cycles (Fig. 1), thereby meeting the goal set for FY2001, while those prepared by low temperature methods and annealed at  $200^\circ\text{C}$  typically delivered only 100 mAh/g. The lower capacities of the latter-type electrodes have been attributed to a difference in crystal morphology of the electrodes.



**Further plans to meet or exceed milestones:** A collaboration with US industry was established during 2001 to investigate the thermal properties of  $\text{InSb}$  electrodes in lithium cells.

**Reason for changes from original milestones:** N/A

## TASK STATUS REPORT

**PI, INSTITUTION:** M.S. Whittingham, SUNY at Binghamton

**TASK TITLE - PROJECT:** Anodes - Novel Materials

**SYSTEMS:** Low-Cost Li-Ion Battery and Gel Battery.

**BARRIER:** Cost, safety and volumetric capacity limitations of lithium-ion batteries

**OBJECTIVES:** To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte.

**APPROACH:** Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

**STATUS OCT. 1, 2000:** We have determined that vanadium and manganese oxides, in their highest oxidation states, are probably not prime candidates. Pure aluminum was found to have a high capacity and to react readily with Li, but its capacity faded rapidly on cycling. Some simple binary alloys of aluminum and of tin have been identified and are being evaluated.

**STATUS SEPT. 30, 2001:** We expect to improve the electrochemical performance of the materials identified, to have completed a survey of all Al-based binary systems and their reactivity with Li, and to have identified several additional non-Al binary alloys. We will complete a study of the lower-valent  $\text{MnV}_2\text{O}_5$  oxide.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONES:** Our major milestone is to identify, by September 2001, a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 V relative to pure Li. In addition, we will identify all known Al binary alloys and their ability to react with Li by August 2001, and our assessment of  $\text{MnV}_2\text{O}_5$  as an anode material will be completed by April 2001.

## PROGRESS TOWARD MILESTONES

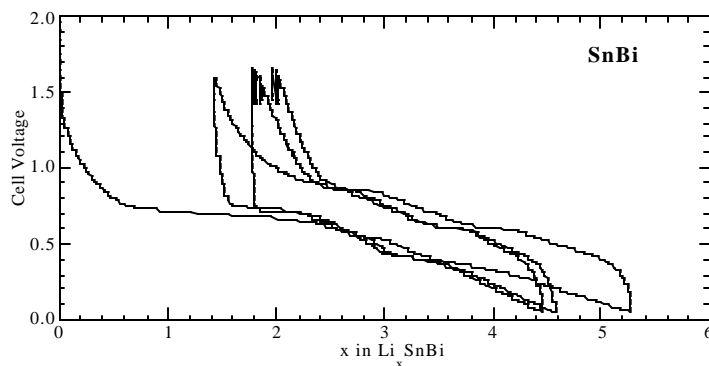
- **Accomplishments toward milestone over last quarter**

We have completed our studies of the oxides based on manganese and iron. Our conclusions are that these materials have insufficient capacity at a potential of interest (  $\sim 1$  volt) for anode use. This is contrary to reports by two French groups and a Japanese group who are strongly promoting phases such as Brannerite,  $\text{MnV}_2\text{O}_6$ .

As reported at the review meeting in June, we have found that aluminum-based anodes do not cycle well in carbonate-based electrolytes. This contrasts with their behavior when in contact with ether-based electrolytes. Our survey of the literature on aluminum systems is almost complete.

As agreed in the AOP we are now generating a plan to build a better understanding for the capacity loss in simple binary metal systems, such as  $\text{MnSn}_2$ , which cycles well for a few cycles then decays rapidly.

There is a large effort at Binghamton investigating lead-free solders for electronics packaging applications. We are beginning discussions with them on their tin-based solders that might possibly lead to attractive tin-based anode materials. One such material is shown below; although not practical this example shows that the new solders might have promise.



**Figure 1.** Cycling of a Sn-Bi solder.

- **Further plans to meet or exceed milestones:** None.
- **Reason for changes from original milestones:** N/A

### Presentations

Solid State Ionics meeting in Cairns, Australia

Three presentations in Taiwan at Synergy Corporation (Lithium Battery Company), ITR National Lab, and Tamsui International Chemistry Frontiers Symposium – September 2001, on “Insertion Electrodes”



## BATT TASK 3 ELECTROLYTES

### TASK STATUS REPORT

**PI, INSTITUTION:** J. Kerr, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Electrolytes - R&D for Advanced Lithium Batteries

**SYSTEMS:** Li/Polymer and Low-Cost Li-Ion

**BARRIERS:** Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities as a result of polymer instability to 4-V cathodes.

**OBJECTIVES:**

- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (4 V) and develop materials and methods to increase stability.

**APPROACH:** Through a balance of synthesis, analysis, and modeling, a physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but the problem can be corrected through the materials design and synthesis capabilities thereby developed.

**STATUS OCT. 1, 2000:** Polymer synthesis capability has been established that facilitates the production of linear and branched polymer networks for use in Li/polymer batteries and polymer gel Li-ion systems. New polymers with significantly higher conductivities are now available as are polymer systems with higher voltage stabilities than PEO.

**STATUS SEPT. 30, 2001:** We have completed a qualitative study of the effects of mechanical, chemical, and transport properties of polymer electrolytes on dendrite growth at Li metal electrodes to provide data to model the system. We have prepared and tested polymer electrolytes with near room-temperature performance and have defined the upper limits of ion transport for normal polymer electrolytes. We plan to determine the practical cathodic stabilities of polymer electrolytes with adequate transport properties.

**RELEVANT USABC GOALS:** 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

**MILESTONES:**

1. Determine electrolyte properties that inhibit dendrite growth (September 30, 2001)
2. Determine the limits of Li ion mobility in polymer electrolytes (September 30, 2001)
3. Prepare bulk materials (100g) for testing in the BATT Li polymer (April 15, 2001) and low-cost Li-ion test systems (June 30, 2001).

## PROGRESS TOWARD MILESTONES

**1. Accomplishments toward milestone over last quarter:** Dendrite growth studies have been completed for several electrolyte systems in symmetrical lithium/lithium cells ( $1\text{ cm}^2$  and  $4\text{ m}^2$  electrode areas) and in  $\text{Li}/\text{V}_6\text{O}_{13}$  cells ( $1\text{ cm}^2$  electrode area). Purified PEO samples of different molecular weights were investigated in  $\text{V}_6\text{O}_{13}$  cells. Rapid fading of cathode capacity was also accompanied by dendrite formation on charge. PEGDME250–LiTFSI electrolytes containing hydrophobic fumed silica (R805), linear PEO (oxymethylene-linked PEG 400) and cross-linked polyepoxy ether comb-branch electrolytes were tested in symmetrical lithium-lithium cells. Dendrite growth was observed in all cases but the nature and rate of onset was different depending on the mechanical properties. The cross-linked polymers exhibit sudden and complete short-circuits of the cells that do not appear to depend on separator thickness. Dendrite growth is inhibited by larger elastic moduli ( $>1\text{MPa}$ ). All of the other polymers are, in effect, viscous liquids that flow under pressure. The dendrite growth for these materials causes voltage fluctuations and apparent electrode area changes. The dendrite growth also occurs at current densities well below the limiting current, in some cases at values around 10% of the  $I_L$ . It has also been noted that failure of cell integrity contributes to the problem as post-mortem analysis reveals the presence of lithium nitride in such cases.

The qualitative conclusions regarding factors that influence dendrite growth are that electrolyte purity and mechanical strength appear to be most critical. The number of coulombs passed prior to current reversal is also critical. Low capacity cycling ( $<0.5\text{ C}/\text{cm}^2$  per cycle) delays the onset of dendrite growth. There is a relationship to the transport properties but this is still not well defined in a quantitative fashion and this is also affected by the cycle capacity. It is noted that a single-ion conductor material was cycled on lithium for  $>8\text{C}/\text{cm}^2$  (USABC goal) with no apparent dendrite growth.

- **Further plans to meet or exceed milestones:** Preparation, quantitative characterization, and testing of cross-linked polymer membranes to determine how transport properties, mechanical properties, and chemical reactivity promotes or inhibits dendrite growth. Three methods of cross-linking will be explored: hydrosilation of allyl ether functions, UV or thermal curing of ether functions and addition of fumed silica to linear polymers (PEO).

- **Reason for changes from original milestone:** The milestone has been met in the qualitative sense in that the major factors that influence dendrite growth have been elucidated. Quantitative confirmation was too ambitious for this year and this will be the primary goal for FY2002

**2. Accomplishments toward milestone over last quarter:** It has been confirmed that the poor kinetic lability of ether-based polymers provides a rate-determining barrier to lithium mobility. Five different polymers have been prepared that contain propanediol or trimethylene oxide (TMO) units. Conductivity measurements indicate that the TMO-containing polymers bind lithium ions less strongly than ethylene oxide polymers. However, the polymer architectures also contain propylene oxide or acrylate units for mechanical purposes and these units bind the lithium ion strongly enough to reduce the ionic mobility and act as coulombic traps.

- **Further plans to meet or exceed milestones:** Synthesis of polymers that do not contain the propylene oxide coulombic trap is under way. Collaboration with modeling groups in the BATT program and in the Office of Science program indicates that the approach will result in polymer electrolytes with room-temperature performance once the interfering coulombic traps are removed.

- **Reason for changes from original milestone:** This milestone is complete, as we have identified the structural features that limit the transport properties of the lithium ion. Polymers that do not contain

these structures are under construction. It is also noted that propylene oxide units limit the cathodic stability and removal of such units is desirable. This conclusion has significant consequences for the design of new polymer electrolytes as it implies that conventional polymer architectures are unsuitable.

**3. Accomplishments toward milestone over last quarter:** Large amounts (>100gm each) of cross-linkable linear and comb polymers have been prepared for testing in the BATT Li/polymer system and the low-cost polymer gel system. Experiments are presently under way to optimize the curing processes to give the desired mechanical properties. Samples of PEO have also been obtained from manufacturers and experiments to improve mechanical properties are ongoing.

- **Further plans to meet or exceed milestones:** Polymers electrolytes will be formulated with salts and electrode components to provide separators and composite electrodes. Appropriate transport and mechanical characterization will be carried out in addition to electrochemical cell testing in Li/V<sub>6</sub>O<sub>13</sub> cells. Cell testing with LiFePO<sub>4</sub> and Li<sub>x</sub>MnO<sub>2</sub> cathodes is planned due to the V<sub>6</sub>O<sub>13</sub> capacity fade. Scale up to an appropriate cell size (e.g., 10-100cm<sup>2</sup> area) is planned.

- **Reason for changes from original milestone:** Staff shortages and unexpected cross-linking of polymers have impeded progress. The latter problem appears to be under control. Collaboration with a polymer manufacturer has been initiated to provide cross-linked PEO materials in large quantities. This addresses the first problem and the milestone is now close to completion (expected December 2001).

## TASK STATUS REPORT

**PI, INSTITUTION:** S.A. Khan, P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

**TASK TITLE - PROJECT:** Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

**SYSTEMS:** Li/Polymer

**BARRIER:** Short lithium battery lifetimes and high costs.

**OBJECTIVES:** The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

**APPROACH:** Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We intend to correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data to be collected include modulus, ionic conductivity, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

**STATUS OCT. 1, 2000:** We established that fumed silica-based composite electrolytes with low-molecular weight PEOs exhibit conductivities exceeding  $10^{-3}$  S/cm at 25°C; have electrochemical properties (Li transference number, conductivity) decoupled from mechanical properties, thus providing a range of mechanical modulus (as high as  $10^6$  Pa); and, the presence of fumed silica enhances Li-electrolyte interfacial stability, although the extent and mechanism remain to be determined.

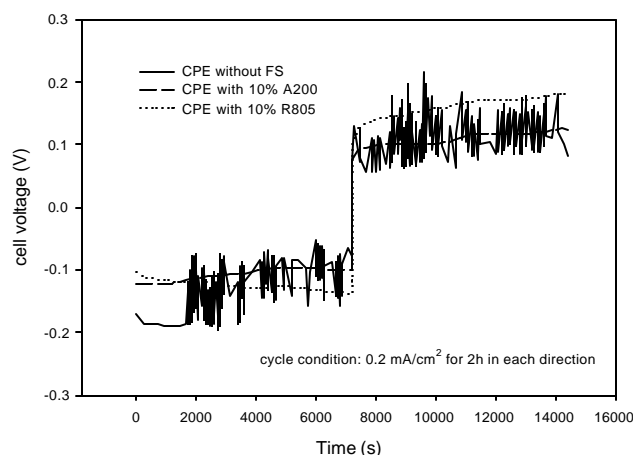
**STATUS SEPT. 30, 2001:** We have determined the effect of fumed silica (hydrophobic R805 and hydrophilic A200) on full-cell cycling using vanadium-based, 3-V cathodes. We have identified to what extent fumed silica enhances interfacial stability in low-molecular weight PEOs. We have begun to characterize how interfacial stability is related to the mechanical properties.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONE:** Our major milestone to determine the effects of fumed silica (hydrophobic R805 and hydrophilic A200) on full-cell cycling and interfacial stability is expected to be completed by September 2001.

## PROGRESS TOWARD MILESTONES

### Accomplishments toward milestone over last quarter:



**Figure 1.** Typical cycling voltage behavior of Li/Li cell with different composite polymer electrolytes (CPEs) with PEGdm (MW 250) + LiTFSI + fumed silica (FS).

We demonstrated that adding fumed silica (FS) attenuates lithium dendrite formation. Lithium dendrites formed for the base-liquid electrolyte after passing only  $0.34 \text{ C/cm}^2$  without fumed silica (Fig. 1); however, the voltage behavior of the CPEs with 10% A200 or 10% R805 does not indicate lithium dendrite formation during cycling. Also, after 20 cycles the interfacial resistance of the CPE was lower than that of the base-liquid.

We have been establishing and optimizing the compositions of vanadium oxide cathodes for use with our electrolytes. Our

vanadium oxide cathodes consist of 75 wt%  $\text{V}_6\text{O}_{13}$  (Kerr-McGee), 10 wt% graphite (Timcal American), 5 wt% Ketjen-Black600 (Akzo Nobel), and 10 wt% binder poly(vinylidene difluoride) (KYNAR). Aluminum foil is used as current collector. In the full-cell Li/CPE/ $\text{V}_6\text{O}_{13}$  system, we have found: 1) Self-discharge performance improves considerably by adding fumed silica, e.g., after full charge to 3.0 V followed by 30-day storage at open circuit, the capacity fades 12% in the absence of fumed silica but only 2% in its presence; 2) Cycle performance improves with addition of fumed silica, e.g., upon cycling at C/15 (C as 417 mAh/g) from 1.8 to 3.0 V at room temperature, the capacity drops after 20 cycles from 300 to 130 mAh/g in the absence of fumed silica but reaches 211 and 203 mAh/g in the presence of 10% A200 and R805, respectively; and, 3) Coulombic efficiency and energy efficiency increase with fumed silica present, e.g., average coulombic efficiency for the first 20 cycles at the above conditions increased from 98.8% without fumed silica to 99.1% with 10% A200, and the average energy efficiency improved from 88.4% to 91.8%.

Although the conductivity is essentially independent of the type of surface group present on the silica, different groups have varied improvement on electrochemical performance in both half- and full-cell studies. Fumed silica A200 having 100% hydrophilic silanol surface groups exhibits better electrochemical performance than R805 having 48% hydrophobic octyl surface groups. A manuscript is under preparation for submission to the *Journal of Electrochemical Society* that discusses our results.

**Further plans to meet or exceed milestone:** We will begin our efforts using LBNL base-line high-MW PEO polymers and fumed silica with different surface groups. In conjunction with Kerr, we will focus on correlating mechanical properties to interfacial stability.

- **Reason for changes from original milestone:** N/A

## TASK STATUS REPORT

**PI, INSTITUTION:** D.F. Shriver, S. Vaynman, Northwestern University

**TASK TITLE - PROJECT:** Electrolytes - Highly Conductive Polyelectrolyte-Containing Rigid Polymers

**SYSTEMS:** Li/Polymer

**BARRIER:** Low ionic conductivity of the polymer electrolyte, electrochemical instability of the polymer electrolyte toward Li electrodes.

**OBJECTIVES:** The primary objective is to synthesize and test a new class of highly ionic-conductive, rigid polymer electrolytes for rechargeable Li batteries.

**APPROACH:** Our approach is to modify the highly ion-conductive rigid polymer electrolytes previously synthesized at Northwestern University by replacing electrochemically unstable carboxy groups with more inert oxygen-rich functional groups such as sulfones, thus increasing the stability of the electrolyte toward the Li electrode. If this or related instabilities with sulfone-containing polymer electrolytes are encountered, we will prepare new polymer electrolytes. One such possibility is a bilayer electrolyte with an oxidation-resistant fluorocarbon backbone on one side and a reduction-resistant hydrocarbon or hydrocarbon ether backbone on the surface in contact with the Li electrode. At least two polymer-salt complexes and polyelectrolytes will be synthesized, and their properties will be measured. These electrolytes will be tested in Li cells. Before polymers are synthesized we will test the stability of the small-molecule analogs of the polymers in contact with Li metal.

**STATUS OCT. 1, 2000:** We synthesized highly conductive rigid polymer electrolytes that contain functional groups such as carboxy and sulfone and tested them in cells. Polymer-salt complexes that contain carboxy groups have high ionic conductivity ( $\sim 10^{-4}$  S/cm at room temperature), but are unstable toward Li. The ionic conductivity of a recently synthesized polymer-salt complex that contains sulfone functional groups is lower ( $\sim 5 \times 10^{-6}$  S/cm at room temperature), but the stability toward Li is much higher than that of polymer-salt complexes that contain carboxy groups.

**STATUS SEPT. 30, 2001:** We synthesized and tested in cells sulfone-containing rigid polymer electrolytes. One of the polymer electrolytes had ionic conductivity at room temperature approaching  $10^{-4}$  S/cm.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONES:** Our major milestones are:

1. To synthesize and test promising polymer systems by 6/2001 with the goal of conductivity higher than  $10^{-4}$  S/cm at room temperature. The resistivity of the Li/polymer electrolyte cell should not increase by more than twice during the first week of testing.
2. To scale-up the synthesis of the most promising polymer electrolyte and to send it by 10/2001 to LBNL for cell fabrication and testing.

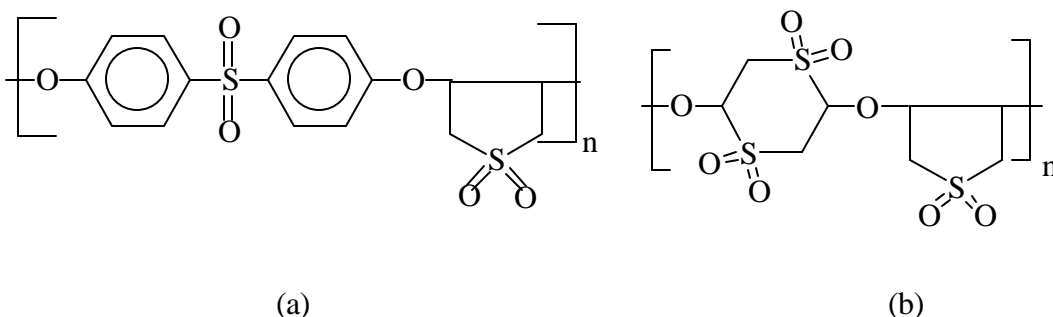
## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:**

Our project focused on:

- a. chemical synthesis of highly ion-conductive rigid polymer electrolytes,
- b. study of the ion-transport properties of these electrolytes,
- c. investigation of interactions at the Li electrode/polymer electrolyte interface,
- d. testing of the electrolyte in a battery configuration.

During the last two quarters we synthesized polysulfones (a) and (b) (Fig. 1). The conductivity of the polysulfone (a) was approximately  $5 \times 10^{-6}$  S/cm at room temperature. This conductivity is lower than we anticipated. The conductivity of a rigid polymer-salt complex that contained carboxy groups (synthesized previously at Northwestern University) had higher ionic conductivity (ca.  $10^{-4}$  S/cm at room temperature) but was unstable toward lithium metal. The polysulfone (a)-salt complex was much more stable toward lithium anode than the complex containing carboxy groups. However, due to low ionic conductivity of electrolyte, the capacity of the cells containing the polysulfone (a) - lithium triflate polymer electrolyte was low.



**Figure 1.** Structure of polysulfones under investigation.

The sulfone-containing polymer (b), which has a higher density of cation coordinating sites than polysulfone (a) (Fig. 1) was synthesized. As expected when doped with lithium triflate in 2:1 molecular ratio, polymer (b) displayed much higher ionic conductivity (approximately  $10^{-4}$  S/cm at room temperature) than polymer (a). This polymer-salt electrolyte was retested after 2 weeks storage in the glove box and the ionic conductivity was significantly lower. We suspect the decomposition or contamination to be reasons for such dramatic property changes. At the present time we are in the process of synthesizing of a new batch of the polymer. When synthesized, the conductivity measurements will be repeated and the stability of it will be investigated.

- **Further plans to meet or exceed milestones:** We did not meet our prior milestones because the synthesized sulfone-containing polymer (b) lost its high conductivity during storage. A new batch of the polymer is synthesized. The ionic conductivity will be measured as a function of time, to determine its stability. If polymer electrolyte is stable, it will be tested in a Li/polymer electrolyte/ $\text{Li}_x\text{MnO}_2$  cell.
- **Reason for changes from original milestones:** Reasons for changes from the original milestones are given above. The contract runs through February 2002 and over this period of time the synthesis and testing of polymer electrolytes will continue. A final report will be prepared in February 2002.

## TASK STATUS REPORT

**PI, INSTITUTION:** K. Kinoshita, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Electrolytes - Electrolyte Additives

**SYSTEMS:** Low-Cost Li-Ion

**BARRIER:** Safety of Li-Ion Batteries

**OBJECTIVES:** The primary objective is to identify chemical additives that improve the safety of nonaqueous electrolytes for Li-ion batteries by stabilizing the SEI layer on carbon.

**APPROACH:** A study will be undertaken to identify suitable additives that function as a radical trap for the radical anions produced by solvent reduction. We propose to use this concept to identify species that are incorporated in the SEI layer to improve its stability. This type of reaction product will be evaluated as additives in gel and liquid electrolytes. Based on our studies of reaction products obtained by thermal decomposition of the electrolyte, compounds that decompose to form polyether and polycarbonate oligomers will be studied as additives. Electrochemical evaluation of additives to determine the reversible and irreversible capacity loss will be conducted in coin cells using the baseline liquid or gel electrolytes. TEM and AFM will be used to study the effect of additives on the thickness and structure of the SEI layer and the irreversible capacity loss of carbon electrodes. Thermal analysis studies will be used to determine the thermal stability of carbon electrodes containing a SEI layer.

**STATUS OCT. 1, 2000:** Experiments were initiated to determine the thermal stability of a baseline electrolyte [1 M LiPF<sub>6</sub> in a mixture of 1:1 EC/DMC]. The electrolyte was heated to 85°C, and samples were removed periodically for analysis by gas chromatography (GC). The GC trace from the electrolyte mixture shows two clearly separate solvent peaks for DMC (5-min retention time) and EC (about 14.1-min retention time) as well as a large new peak at 13.8-min retention time and several others of lower intensity. The peak intensity for EC decreases as a function of storage time, indicative of the gradual decomposition of EC at 85°C. On the other hand, the GC signal for DMC remains essentially constant in intensity, indicating that DMC is stable during storage at 85°C. The major new compound was identified as diethyl 2,5 dioxahexane carboxylate (DEDOHC), which increases with time of storage at 85°C.

**STATUS SEPT. 30, 2001:** The polyether carbonates [PE<sub>3</sub>C] were identified as possible decomposition products in 1 M LiPF<sub>6</sub>/1:1 EC/DMC heated to 85°C. Our expectations were that they should have a beneficial role in the properties of the SEI layer on graphite electrodes. However, adding PE<sub>3</sub>C to the electrolyte had no benefit in reducing the irreversible capacity loss or the structure of the SEI layer.

**RELEVANT USABC GOALS:** Identify additives that improve the safety of Li-ion batteries.

### MILESTONES:

1. Identify desired structural features of additives that enhance SEI properties (12/00).
2. Evaluate the effect of polycarbonates as additives for improving the thermal stability of the SEI layer on carbon electrodes (9/01).



## PROGRESS TOWARD MILESTONES

The role of additives and their effect on the properties of the SEI layer on carbon are the focus of this study. Evidence obtained by Sloop et al. [S.E. Sloop, J.K. Pugh, S. Wang, J.B. Kerr and K. Kinoshita, *Electrochem. Solid-State Lett.*, **4**, A42 (2001)] suggested that an organic base in the electrolyte reduces the decomposition rate of EC/DMC by limiting the disproportionation of  $\text{LiPF}_6$ . With this in mind, we initiated electrochemical studies of carbon electrodes in EC/DMC electrolyte containing organic bases such as pyrrole and pyridine. We are interested in determining the electrochemical reduction properties of the N-containing aromatic compounds, and their effect on the irreversible capacity loss of graphite electrodes.

Cyclic voltammetry (CV) was used to observe differences in the current-potential profiles of graphite electrodes (Gen 2) in electrolytes [1 M  $\text{LiPF}_6$ /EC-DMC (LP30) and 1 M  $\text{LiPF}_6$ /EC-EMC (Gen 2)] with and without the addition of pyrrole and pyridine. The initial cathodic scan at 1 mV/s showed only minor variations in the current-potential profiles from open circuit (i.e., about 3 V) to 0.01 V (vs. Li). There was evidence for low cathodic currents in the vicinity of 1.5-2.0 V when pyrrole was present in the electrolyte. There appears to be a slight increase in the current of Gen 2 electrodes when 0.1 M pyrrole was present in the electrolytes, which may be due to reduction of pyrrole. The CV results show that the peak current for deintercalation in the cyclic voltammogram is about 77% and 40% higher, respectively, when 0.1 M pyrrole is added to the electrolyte. The significance of this finding is not clearly understood but it may be associated with changes in the properties of the SEI layer or reactions involving pyrrole. Further studies are underway.

- **Accomplishments toward milestone 1 over last quarter:**

Complete. Described in FY01 first quarterly report.

- **Further plans to meet or exceed milestone:** None
- **Reason for changes from original milestone:** N/A

- **Accomplishments toward milestone 2 over last quarter:**

A postdoctoral fellow was hired, but he left after about six weeks to accept a permanent position in Korea. Further effort on this milestone has stopped until a new postdoctoral fellow arrives.

- **Further plans to meet or exceed milestone:**

Experiments will be conducted with additives that are expected to decompose during the initial intercalation (charge) of carbon electrodes in the baseline electrolyte. The addition of  $\text{PE}_3\text{C}$  to the electrolyte has so far not provided evidence that it has a beneficial effect on the irreversible capacity loss or the structure of the SEI layer. However the thermal stability of the SEI layer formed with the  $\text{PE}_3\text{C}$  additive in the electrolyte has not been investigated. Thermal studies will be considered when a postdoctoral fellow arrives.

- **Reason for changes from original milestone:** N/A

## TASK STATUS REPORT

**PI, INSTITUTION:** J. Prakash, Illinois Institute of Technology

**TASK TITLE - PROJECT:** Electrolytes - Nonflammable Electrolytes and Thermal Characterization

**SYSTEMS:** Li/Polymer and Low-Cost Li-Ion

**BARRIER:** Thermal safety

**OBJECTIVES:** The goal of this proposal is to assist DOE/BATT in developing advanced high-performance Li-ion cells for electric and hybrid vehicles. The objectives of this project are: (1) to develop nonflammable electrolytes with high flash point ( $>100^{\circ}\text{C}$ ), ionic conductivity ( $10^{-3}$  S/cm), and wider voltage window (0-5 V vs. Li); and (2) to evaluate anode and cathode (being developed in the BATT Program) materials in coin cells using thermal diagnostic methods.

**APPROACH:** Our research approach will include (1) the development of thermally stable and nonflammable electrolytes to provide safety and (2) thermal diagnostic studies of the baseline Li-polymer and low-cost Li-ion cells using differential scanning calorimetry (DSC), isothermal microcalorimetry (IMC), and accelerated rate calorimetry (ARC) in order to understand the degradation, failure, and safety mechanisms.

**STATUS OCT. 1, 2000:** We completed the synthesis of the flame retardant (FR) hexa-methoxy-tri-aza-phosphazene  $\text{N}_3\text{P}_3[\text{OCH}_3]_6$  and supplied 10 grams of this material to the ATD Program (ANL and PolyStor) for further testing in PNGV Li-ion cells. We also completed the thermal and electrochemical characterization of this FR additive in Li-ion cells using cyclic voltammetry, AC-impedance, cell cycling, DSC, and ARC.

**STATUS SEPT. 30, 2001:** We successfully scaled-up the synthesis of the flame retardant (FR) HMTAP to produce about 25 g sample in a single batch and supplied this material to the ANL and Quallion for further testing in PNGV Li-ion cells. We also completed the initial thermal and electrochemical characterization of a new FR additive HETAP in Li-ion cells using cyclic voltammetry, AC-impedance, cell cycling, DSC, and ARC. In addition, we also completed the mechanistic studies of the interaction of the FR additive HMTAP with the anode in Li-ion cells and proposed the  $\text{Li-P}(\text{OCH}_3)_2$  adsorbed on the electrode surface.

**RELEVANT USABC GOALS:** Thermal and fire safety of the EV batteries under normal and abusive conditions.

**MILESTONES:** The electrochemical and thermal characterization of the new flame retardant HETAP in Gen-2 Li-ion cells will be completed by the end of December 2001. The thermal characterization of the Li-ion cells with EC-EMC/ $\text{LiPF}_6$  electrolyte using IMC and DSC will also be completed by the end of December 2001.

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:** 1. During this reporting period, we completed the synthesis of a new FR flame retardant (HETAP) and characterized this additive for its electrochemical and thermal properties using cyclic voltammetry, AC-impedance, and accelerated rate calorimetry (ARC) in EC-DMC/LiPF<sub>6</sub> liquid electrolyte. Initial thermal behavior of the new FR additive looks promising and we will be investigating the performance of the Li-ion cells containing this additive in the coming months.

In an effort to understand the mechanism of action, we carried out spectroscopic studies of the graphite anode surface using <sup>1</sup>H NMR and <sup>31</sup>P NMR (Fig. 1) and FTIR after being exposed to the electrolyte containing the FR additive. Results of our spectroscopic studies carried out on the electrodes removed from the Li-ion cells fabricated with the FR additive HMTAP showed the presence of Li-P(OCH<sub>3</sub>)<sub>2</sub> species on the electrode surface. The -P(OCH<sub>3</sub>)<sub>2</sub> group has been proposed to provide the thermal safety and flame retardancy.

We are also carrying out the thermal characterization of PNGV Gen-2 cells using the Isothermal Microcalorimetry, Differential Calorimetry, and Accelerated Rate Calorimetry (Task-2 - FY 2001). These studies were aimed at studying the thermal effects under normal conditions and quantifying the contributions of the cell components to the heat effects, and the development of an effective protocol (diagnostics) for further testing. The interpretation of the data is currently in progress.

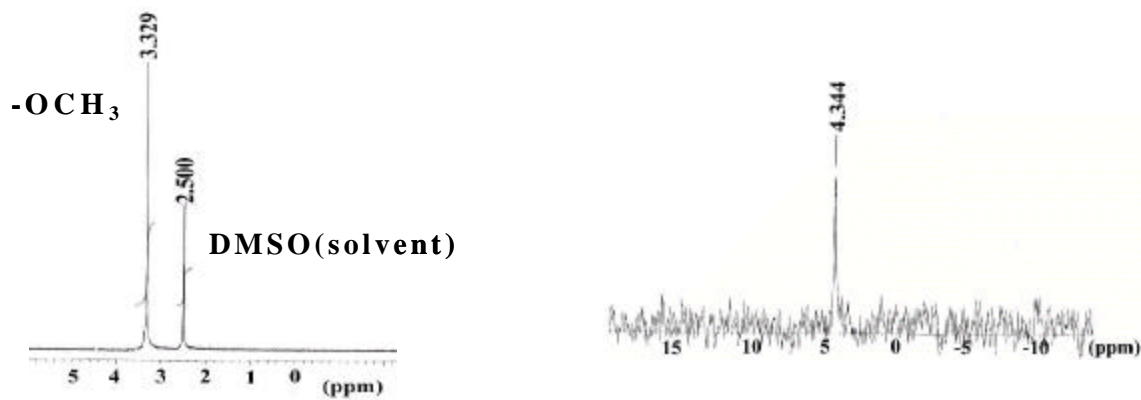


Figure 1. <sup>1</sup>H NMR (left) and <sup>31</sup>P NMR (right) spectra of a carbon electrode subjected to a cathodic potential of 10 mV vs. Li for 3 hours

- **Further plans to meet or exceed milestone:** We plan to complete the electrochemical investigations as well as mechanistic studies of the additive HETAP in Li-ion cells in order to understand the catalytic reaction of the FR additive with the electrode/electrolyte especially at higher temperatures. We will complete the thermal characterization of PNGV Gen-2 cells (for future BATT use) using isothermal microcalorimetry and DSC.
- **Reason for changes from original milestone:** This project is being discontinued and we will change our strategy accordingly in order to complete this project successfully. Our previous investigations have shown that the presence of FR additive HMTAP increases the onset of the thermal runaway of the Li-ion cells by more than 25°C, which is encouraging for the safety. However, the SHR at temperatures beyond 265°C was found to increase in presence of HMTAP. In order to address the issue of SHR at higher temperatures and to complete this project, we will investigate the synthesized FR additive (HETAP) for its viability as a FR additive in the Li-ion cells.

**Presentation:** “Studies on electrochemical and thermal properties of Li-ion battery electrolytes with different salts” at the Phoenix ECS Meeting (Abst. 143).

## BATT TASK 4 CATHODES

### TASK STATUS REPORT

**PI, INSTITUTION:** M. Thackeray, Argonne National Laboratory

**TASK TITLE:** Cathodes - Novel Materials

**SYSTEMS:** Low-Cost (Li-Ion) Battery and Li-Polymer Battery

**BARRIER:** Cost limitations of Li-ion and Li-polymer batteries

**OBJECTIVES:** To develop low-cost manganese-oxide cathodes to replace vanadium oxide electrodes in Li-polymer cells and cobalt/nickel electrodes in Li-ion cells.

**APPROACH:** Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes that can be used in Li-ion and Li-polymer cells; the electrodes will be synthesized in the discharged and charged states, respectively. For Li-ion cells, focus will be placed on layered lithium-manganese oxide structures that do not convert to spinel upon electrochemical cycling, particularly those derived from  $\text{Li}_2\text{MnO}_3$ ; for Li-polymer cells, the material of choice is stabilized  $\alpha\text{-MnO}_2$ . (Note: At this stage of the project, we have downgraded the research priority to search for an alternative vanadium oxide electrode, such as  $\text{V}_6\text{O}_{13}$ , to replace the current material of choice,  $\text{LiV}_3\text{O}_8$ , because in the Li-V-O system,  $\text{LiV}_3\text{O}_8$  is still believed to be the best vanadium oxide electrode available for Li-polymer cells.)

**STATUS OCT. 1, 2000:** We have exploited the concept of using a  $\text{Li}_2\text{MnO}_3$  component to stabilize layered  $\text{LiMO}_2$  structures with the ultimate objective of stabilizing layered  $\text{LiMnO}_2$ . In particular, we expanded our synthesis efforts to include solid solutions of  $[\text{x}(\text{Li}_2\text{MnO}_3)\cdot\text{y}(\text{LiMO}_2)]$  compositions, where  $\text{M} = \text{Mn, Ni or Co}$ , or a combination thereof. Optimized compositions have yielded specific capacities of  $\sim 150$  mAh/g between 4.5 and 3.0 V in Li half-cells at  $50^\circ\text{C}$ , but for less than 100 cycles.

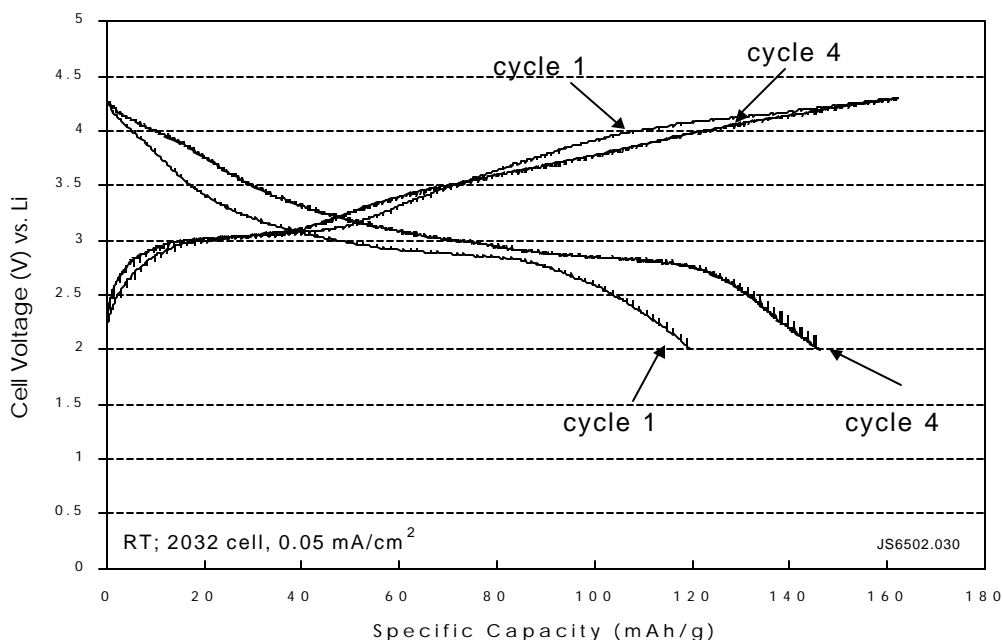
**STATUS SEPT. 30, 2001:** Improvements in the electrochemical performance of  $[\text{x}(\text{Li}_2\text{MnO}_3)\cdot\text{y}(\text{LiMO}_2)]$  electrodes will have been achieved. A performance target of 150 mAh/g for 100 cycles at  $50^\circ\text{C}$  in Li/ $[\text{x}(\text{Li}_2\text{MnO}_3)\cdot\text{y}(\text{LiMO}_2)]$  cells has been set. A more detailed understanding of the behavior of  $[\text{x}(\text{Li}_2\text{MnO}_3)\cdot\text{y}(\text{LiMO}_2)]$  electrodes will have been gathered. Work on stabilized  $\alpha\text{-MnO}_2$  electrodes for Li-polymer cells will have been initiated in collaboration with LBNL (J. Kerr) with an initial target reversible capacity set at 200 mAh/g for 50 cycles.

**RELEVANT USABC GOALS:** 10-year life,  $<20\%$  fade over a 10-year period.

**MILESTONES:** The initial milestone (#1) to be reached by the end of April 2001 will be to achieve a reversible electrochemical capacity of 150 mAh/g from layered  $[\text{x}(\text{Li}_2\text{MnO}_3)\cdot\text{y}(\text{LiMO}_2)]$  electrodes for 50 cycles at  $50^\circ\text{C}$  against a metallic Li counter electrode. This will be increased to 100 cycles by the end of September 2001 (#2). By then a more detailed understanding of the electrochemical and structural relationships of layered  $[\text{x}(\text{Li}_2\text{MnO}_3)\cdot\text{y}(\text{LiMO}_2)]$  electrodes will also have been gathered.

## PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone 1 over last quarter:** Layered and  $\alpha$ - $\text{MnO}_2$  electrodes have been synthesized for Li-polymer cell applications; samples of  $\alpha$ - $\text{MnO}_2$  electrodes have been sent to Hydro-Quebec for preliminary screening. In the last report, we reported the phase diagram of the  $\text{MnO}_2$ - $\text{Li}_2\text{MnO}_3$ - $\text{LiMnO}_2$  system. Layered structures of composition  $\text{Li}_{2-x}\text{MnO}_{3-x/2}$  ( $0 < x < 2$ ) are formed by acid treatment of  $\text{Li}_2\text{MnO}_3$ . Lithiation of these materials yields a composite  $\text{Li}_2\text{MnO}_3 \bullet \text{LiMnO}_2$  structure. The acid treatment process has been monitored by NMR spectroscopy. Results indicate that the lithium is removed from the octahedral sites between the Mn layers of the  $\text{Li}_2\text{MnO}_3$  precursor. However, protons (or  $\text{H}_3\text{O}^+$ ) are also exchanged during this reaction. Figure 1 shows the voltage profiles of the layered  $\text{Li}_{2-x}\text{MnO}_{3-x/2}$  electrode. The electrochemical capacity of the electrode improves on cycling, yielding approximately 145 mAh/g after 4 cycles. We are presently developing a post chemical heat-treatment process at mild temperatures to improve the overall cycling performance of acid-leached  $\text{Li}_{2-x}\text{MnO}_{3-x/2}$  ( $0 < x < 2$ ) electrodes.



**Figure 1.** Voltage profile of a  $\text{Li}/\text{Li}_{2-x}\text{MnO}_{3-x/2}$  cell. Electrochemical cycling was performed at room temperature between 4.3 and 2.0 V.

For Li-ion cells, the layered material  $\text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2$  was successfully synthesized from mixed-metal hydroxide precursors. Indications from the literature suggest that the Ni is divalent and the Mn is tetravalent. Thus, the charge-discharge reaction is due to the  $\text{Ni(II)}/\text{Ni(IV)}$  redox couple. This material has been evaluated in some recently built coin cells at 50 °C with some success. Preliminary data show that after 5 cycles capacities can exceed 150 mAh/g when cells are charged and discharged between 4.3 and 3.0 V. (These experiments are still in progress.) The voltage profile of  $\text{Li}/\text{Li}[\text{Mn}_{0.5}\text{Ni}_{0.5}]\text{O}_2$  cells is smooth, indicating that a single-phase electrochemical reaction occurs at the cathode.

- Further plans to meet or exceed milestones:** None
- Reason for changes from original milestones:** N/A

## TASK STATUS REPORT

**PI, INSTITUTION:** M.S. Whittingham, SUNY at Binghamton

**TASK TITLE - PROJECT:** Cathodes – Novel Materials

**SYSTEMS:** Li/Polymer/Gel and Low-Cost Li-Ion

**BARRIER:** Lower-cost, higher-capacity and safer cathodes

**OBJECTIVES:** The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

**APPROACH:** Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

**STATUS OCT. 1, 2000:** We determined that layered manganese dioxides can be structurally stabilized, that their stability is a function of current density and/or cut-off voltages, that their electronic conductivity can be significantly enhanced, that their cell cycling can be substantially improved by addition of other transition metals, and that hydrothermally synthesized manganese oxides cycle as well as high-temperature materials. We also showed that vanadium oxides can be stabilized by the addition of manganese ions.

**STATUS SEPT. 30, 2001:** For low-cost Li-Ion cells, we expect to identify the changes in  $\text{LiMnO}_2$  structure as a function of current density in cell cycling, to determine the structure and composition of the vanadium-stabilized  $\text{LiMnO}_2$  and to increase its electrochemical capacity, to understand better the behavior of the  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$  cathode and to determine if there is an iron analog. For Li/polymer cells we expect to complete the evaluation of the manganese-stabilized  $\delta$ -vanadium oxides and to compare them to the iron phosphates. Emphasis in all cases will be placed on understanding the reasons for capacity fade.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONES:** Our major milestones this year are:

1. to characterize the pillared manganese oxide, and improve its capacity to 150 mAh/g with an ultimate goal of 200 Ah/kg.
2. to complete the characterization of manganese-stabilized vanadium oxides and to compare the best samples with iron phosphates for polymer or gel batteries by July 2001.

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:** We have explored the formation of the vanadium pillared layered manganese dioxides at lower temperatures. The same phase can be formed as low as 80°C, but it is less crystalline which will make characterization more difficult. Electrochemical evaluation is underway now.

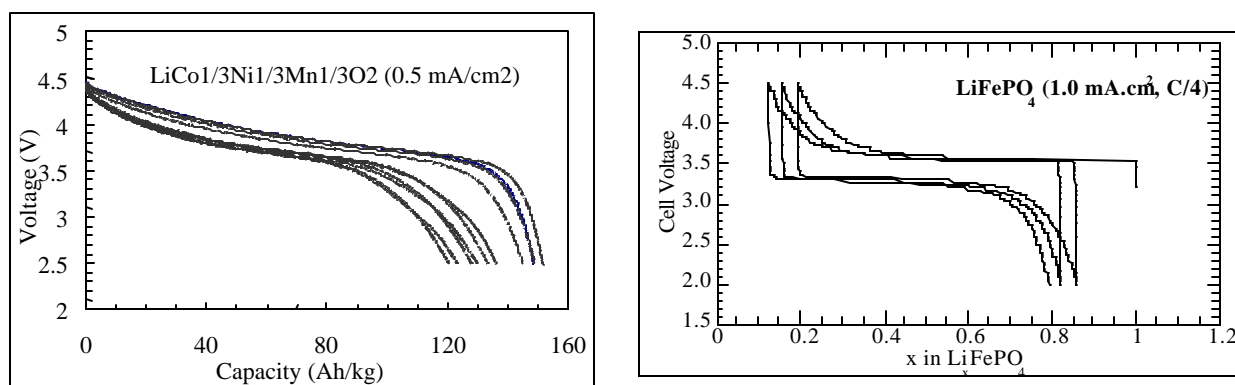
We have prepared a number of analogs of the  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$  cathode and found good cycling behavior for the cobalt and nickel analogs, e.g.  $\text{Li}_{1+x}\text{Ni}_y\text{Co}_z\text{Mn}_{1-x-y-z}\text{O}_2$ . These all showed single phase behavior and cycled well but with some capacity loss on the first cycle.

We have had limited success in substituting iron for chromium in  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$ .

- **Further plans to meet or exceed milestones:** None
- **Reason for changes from original milestones:** N/A
- **Accomplishments toward milestone 2 over last quarter:** We have almost completed the exploration of the hydrothermal method as a low-cost manufacturing process for lithium iron phosphate. The iron phosphate so formed would then be used as a comparison standard for our new cathode program. Crystalline iron phosphate has been formed, characterized and electrochemically evaluated. It has also been carbon coated to increase the particulate conductivity; carbon coating significantly increased the capacity allowing capacities of about 150 Ah/kg to be attained.

The hydrothermal material is not the same as the high-temperature material, but converts to it during the carbon-coating process. The capacity of the hydrothermal material is about 100 Ah/kg prior to coating and 150 Ah/kg after coating. The data obtained using a new coating method are shown below. Amorphous anhydrous  $\text{FePO}_4$  shows good capacity, with a sloping discharge typical of a single-phase system without carbon coating. We are evaluating all iron phosphate phases for stability and electrochemical behavior.

The study of the Mn pillared vanadium oxides is close to completion. These delta vanadium oxides show initial capacities over 200 Ah/kg, but the capacity falls on cycling.



**Figure 1.** High-rate cycling of carbon coated (left)  $\text{Li}_{1+x}\text{Ni}_y\text{Co}_z\text{Mn}_{1-x-y-z}\text{O}_2$  and (right)  $\text{LiFePO}_4$ .

- **Further plans to meet or exceed milestones:** None
- **Reason for changes from original milestones:** N/A

**Publication:** S. Yang, P.Y. Zavalij and M.S. Whittingham: Hydrothermal Synthesis of Lithium Iron Phosphate Cathodes, *Electrochem. Commun.*, **3** (2001) 505-508.

**Presentation:** Sept. 2, 2001. ECS/ISE Meeting, San Francisco CA: Hydrothermal Synthesis and Electrochemical Behavior of Oxide Cathodes for Lithium Batteries.

## TASK STATUS REPORT

**PI, INSTITUTION:** M. Doeff, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium Ion Batteries

**SYSTEMS:** Li/polymer and low-cost Li-ion

**BARRIERS:** Cost, cycle life, safety, and energy density

**OBJECTIVES:** To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

**APPROACH:** Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.*, sol-gel, glycine-nitrate combustion). The microstructures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on structurally stable materials such as tunnel-containing manganese oxides, as well as those of commercial interest, such as spinels and lithium iron phosphate.

**STATUS OCT. 1, 2000:** A tunnel-containing manganese oxide has been cycled more than 700 times in a Li/liquid electrolyte cell configuration, with little capacity loss and no structural change. Cells can be discharged repeatedly at up to 5 C rate with no damage. The effect of Ti-substitution upon the electrochemical characteristics has been determined, and a correlation between unit cell size and capacity has been observed.

**STATUS SEPT. 30, 2001:** The program will be expanded to include lithium iron phosphates and substituted spinels as required by the BATT program. We expect to have prepared samples of  $\text{LiFePO}_4$  available for the program and to have made a preliminary determination of the electrochemical characteristics. We also will have determined if anion substitution of tunnel-containing manganese oxides is a viable approach to improving capacity.

**RELEVANT USABC GOALS:** 10-year life, < 20% capacity fade over a 10-year period.

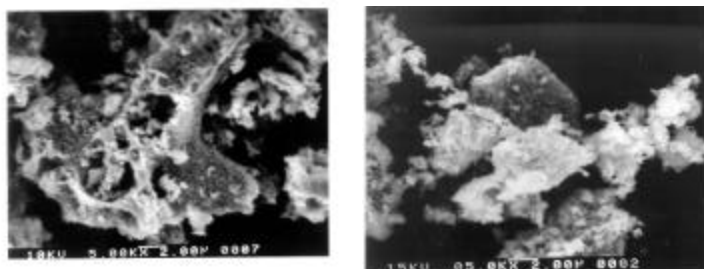
**MILESTONES:** A milestone to provide  $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$  to the BATT program in Fall 2001 was met this quarter.



## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

“ $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$ ” was synthesized by a sol-gel technique outlined in a paper by Park et al. (*J. Electrochem. Soc.*, **147**, 2116 (2000)), and also by a solid-state method. Analogs without sulfur were also prepared by sol-gel and solid-state routes. All materials were determined to be phase-pure by x-ray powder diffraction, and had lattice parameters of 8.19 Å, consistent with Al-substituted lithium manganese oxide spinel. Scanning electron microscopy showed that all samples had essentially the same particle morphology (Fig. 1a). Particles were very porous and lightly fused together due to the long heating regime and the release of  $\text{CO}_2$  gas from decomposition of the acetate precursors. The unusual idiomorphic morphologies shown in Park’s work were not observed, although a few smooth particles were seen in sulfur-containing samples (Fig. 1b). A small amount of sulfur was detected in the smooth particles by electron dispersive spectroscopy (detection limit for sulfur ~1%), but none was seen in the porous particles that formed the bulk. The morphology of the particles is determined by the sulfide ion content in the reaction mixture, but  $\text{Li}_2\text{S}$  oxidizes uncontrollably during synthesis in air and oxygen, making Park’s results difficult to reproduce. Because the as-made sol-gel  $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$  contained large clusters of fused particles, it was ground and sieved (final size about 4  $\mu\text{m}$  in diameter determined by particle size analysis) prior to incorporation into BATT program electrodes (K. Striebel).  $\text{Li}/1\text{M LiPF}_6$ , EC-DMC/ $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$  cells discharge about 80 mAh/g on the 4V plateau at C/4 rate and cycle with a slow capacity loss. When cycled over both the 4 and 3 V plateaus, cells discharge about 130 mAh/g at C/8 rate, with rapid capacity fade, in contrast to Park’s report.



**Figure 1a (left) and 1b (right)** showing particles of sol-gel  $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$ .

- **Further plans to meet or exceed milestones** The synthesis of  $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$  will be repeated, and electrodes containing more carbon will be fabricated to improve utilization and cycling behavior.
- **Reason for changes from original milestones** The original milestone to provide  $\text{LiFePO}_4$  for the BATT program was changed to  $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$  because Hydro-Québec is now supplying  $\text{LiFePO}_4$ .

**Publication:** “Improved Discharge Characteristics of Tunnel-Containing Manganese Oxide Electrodes for Rechargeable Lithium Battery Applications”, M.M. Doeff, T.J. Richardson, K-T. Hwang, and A. Anapolsky, *ITE Battery Lett.*, **Vol.2, No. 3** B-63 (2001).

**Presentation:** “Effect of Ion Substitution on the Electrochemical Characteristics of Tunnel-containing Manganese Oxide Electrodes” M.M. Doeff, T.J. Richardson, M. Gonzales, and K-T. Hwang, presented at the Joint International Meeting of The Electrochemical Society and the International Society of Electrochemistry, September 2001, San Francisco, CA.

## BATT TASK 5 DIAGNOSTICS

### TASK STATUS REPORT

**PI, INSTITUTION:** F. McLarnon, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Electrode Surface Layers

**SYSTEMS:** Li/Polymer and Low-Cost Li-Ion

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVES:** The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity decline.

**APPROACH:** Our approach is to use ellipsometry, Raman spectroscopy, and advanced microscopic techniques to characterize electrodes taken from baseline BATT Program cells, as well as thin-film electrodes in model cells. Data to be collected include changes in electrode surface morphology, electrode surface chemistry, and SEI thickness and composition, which accompany cell cycling.

**STATUS OCT. 1, 2000:** We defined the relationships between electrode history, electrolyte composition, electrode surface properties, and temperature for a model thin-film spinel  $\text{LiMn}_2\text{O}_4$  cathode.

**STATUS SEPT. 30, 2001:** We identified changes in  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathode surface chemistry, which accompanied cycling in  $\text{LiPF}_6$ -EC-EMC electrolyte, and identified surface carbon loss as a potential cell degradation mode.

**RELEVANT USABC GOALS:** 0 year life, < 20% capacity fade over a 10-year period.

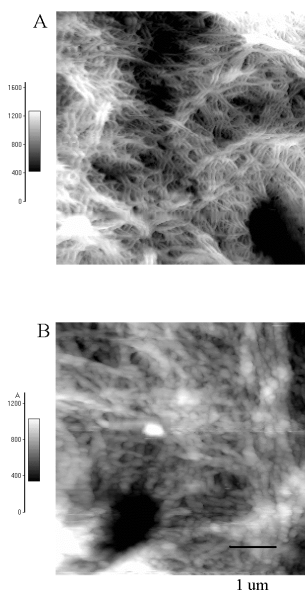
**MILESTONE:** Our major milestone was to determine the effects of added sulfur on the surface chemistry and morphology of  $\text{LiMn}_2\text{O}_4$  electrodes, and it was completed by the planned date of April 2001. To investigate the postulated S-for-O substitution and its effect on the electrochemical properties of manganese spinel electrodes, three types of S-modified electrodes were fabricated by exposing a thin-film  $\text{LiMn}_2\text{O}_4$  electrode to elemental S at 25, 160, and 260°C (we prepared and studied model thin-film electrodes rather than porous electrodes not only because the latter were not available, but also to provide a baseline for porous electrode studies to be conducted in FY 2002). Exposure to S at room temperature produced no effect, whereas exposure to S at elevated temperatures induced significant changes to the electrode morphology and surface composition. The electrode exposed to S at 160°C exhibited good electrochemical cyclability, although its Raman spectrum showed strong fluorescence which originated from Li salt(s). The electrode exposed to S at 260°C displayed no electrochemical activity vs. Li. High surface concentrations of sulfates and sulfites which formed during the reaction between  $\text{LiMn}_2\text{O}_4$  and S were primarily responsible for the observed capacity loss. In conclusion, we determined that bulk substitution of S for O is very unlikely due to the weak bonding energy of S with Mn and the extremely high catalytic activity of  $\text{Mn}^{4+}$  toward S oxidation, however S does appear to modify the electrode surface morphology and chemistry.

## PROGRESS TOWARD MILESTONES

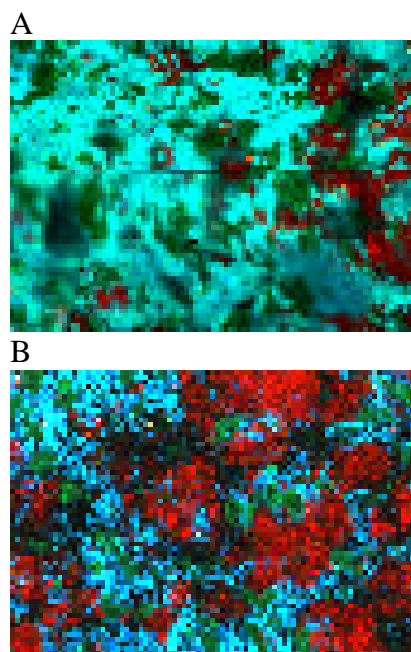
- **Accomplishments toward milestone over last quarter:** Characterization of Doo Youn cells was completed. We used atomic force microscopy (AFM) to study the structural integrity and stability of separators from three Doo Youn cells: two fresh cells, and a cell which was cycled 174 times at room temperature and exhibited 48% power fade at the end of cycling. Figure 1 shows AFM images of these separators. Although the origin and composition of this separator are unknown, it is clear that its morphology changed significantly during cycling. It is difficult to determine to what extent these changes in separator morphology affected battery operation. However, separator degradation has been overlooked as a possible contributor to cell performance decline. We will include separator analysis in our future diagnostic studies of BATT Program cells.

We initiated diagnostic studies of BATT Program baseline cells which were assembled and tested by K. Striebel. We carried out a series of AFM and Raman microscopy measurements of the  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathode from a small 100 mAh cell. The cell was cycled 400 times at room temperature, and it exhibited a significant impedance rise at the end of cycling with almost no capacity fade. AFM images of the cathode after cycling did not reveal significant changes in surface morphology. However, Raman microscopy mapping showed substantial changes in the electrode surface composition. Figure 2 shows Raman image maps of the cathode where colors are assigned to three electrode components: red =  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , green = graphite, and blue = acetylene black. Measurements at different locations confirmed that the surface concentration of carbon was significantly lower in the cycled cathode. Carbon depletion can decrease the electronic conductivity between grains of active material, and thereby lead to the observed increase of cell impedance.

A new spectro-electrochemical cell was designed for *in situ* studies of thin-film electrodes. We will employ it to study surface phenomena at model sulfur-doped  $\text{LiMn}_2\text{O}_4$  spinel and  $\text{LiFePO}_4$  electrodes in the coming weeks.



**Figure 1:** AFM images of separators from Doo Youn cells. A- cycled cell, B - fresh cell



**Figure 2:** Raman maps of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathodes. A -fresh, B -from a cycled cell

- **Further plans to meet or exceed milestones:** None
- **Reason for changes from original milestones:** N/A

## TASK STATUS REPORT

**PI, INSTITUTION:** J. McBreen Brookhaven National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Structure and Characterization of Materials

**SYSTEMS:** Low-Cost Li-Ion

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVES:** The primary objective is to establish direct correlations between electrode materials changes, interfacial phenomena, and cell capacity decline.

**APPROACH:** Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge X-ray absorption spectroscopy and transmission electron microscopy (TEM).

**STATUS OCT. 1, 2000:** We have completed an extensive study of the effect of Li and O stoichiometry on the phase behavior of spinel  $\text{LiMn}_2\text{O}_4$  cathodes during cycling at ambient and at low temperatures. The effects of electrode history on the phase behavior of  $\text{LiMn}_2\text{O}_4$  cathodes were also investigated.

**STATUS SEPT. 30, 2001:** We expect to identify the changes in  $\text{LiNi}_k\text{Mn}_{2-x}\text{O}_2$  and  $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$  when cycled in  $\text{LiPF}_6$ -EC-DMC electrolyte. We also expect to develop a combination of electron yield and fluorescent XAS at transition metal K- and L-edges as a tool for identification of inorganic surface degradation products in cathodes.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

### MILESTONES:

1. Completion of XAS studies of  $\text{LiCrMnO}_2$  by April 2001.
2. Completion of XRD and XAS studies of  $\text{LiNi}_k\text{Mn}_{2-x}\text{O}_4$  by June 2001.
3. Develop a combination of electron yield and fluorescent XAS at transition metal K- and L-edges as a tool for identification of inorganic surface degradation products in cathodes by September 30, 2001.
4. Determine electrolyte effect on stability of  $\text{LiMn}_2\text{O}_4$  at elevated temperatures by December 30, 2001.

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:** A paper on the XAS work on  $\text{LiCrMnO}_2$  has been accepted for publication in the Journal of the Electrochemical Society. This completes milestone (1).
  - **Further plans to meet or exceed milestone:** None.
  - **Reason for changes from original milestone:** N/A
- 
- **Accomplishments toward milestone 2 over last quarter:** The XRD and XAS studies on  $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$  materials ( $x = 0.1, 0.3$  and  $0.5$ ) has been completed and a paper is being prepared for publication. This completes milestone (2).
  - **Further plans to meet or exceed milestone:** None.
  - **Reason for changes from original milestone:** N/A
- 
- **Accomplishments toward milestone 3 over last quarter:** The *ex situ* XAS technique using soft x-rays and a combination of fluorescent x-ray and electron yield techniques has been developed for the study of surface processes on electrodes. The technique has been applied to the identification of electrolyte decomposition products on cathodes in the ATD Program. A paper on the ATD work has been accepted for publication in Electrochemistry and Solid State Letters. This completes milestone (3).
  - **Further plans to meet or exceed milestone:** None.
  - **Reason for changes from original milestone:** N/A
- 
- **Accomplishments toward milestone 4 over last quarter:** Most of the work on milestone (4) has been completed. This has included work on  $\text{LiMn}_2\text{O}_4$  and  $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ . Because of the limited energy density no work will be done on  $\text{Li}_{1.02}\text{Al}_{1.25}\text{Mn}_{1.75}\text{O}_{3.97}\text{S}_{0.03}$ .
  - **Further plans to meet or exceed milestone:** None.
  - **Reason for changes from original milestone:** Because of the limited energy density no work will be done on  $\text{Li}_{1.02}\text{Al}_{1.25}\text{Mn}_{1.75}\text{O}_{3.97}\text{S}_{0.03}$ .
- 
- **Accomplishments toward milestone 5 over last quarter:** The work on milestone (5) is on schedule.
  - **Further plans to meet or exceed milestone:** None.
  - **Reason for changes from original milestone:** N/A

## TASK STATUS REPORT

**PI, INSTITUTION:** P.N. Ross, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics – Interfacial and Reactivity Studies

**SYSTEMS:** Low-Cost Li-Ion

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVES:** The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

**APPROACH:** Our approach is to use Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) to study model electrode/electrolyte combinations, *e.g.*, using glassy carbon electrodes and BATT Program electrolytes, to provide the basis to interpret more-complex spectra recorded for ATD Program cell materials.

**STATUS OCT. 1, 2000:** We identified one of the mechanisms of SEI layer formation on carbon anode in EC-based electrolytes.

**STATUS SEPT. 30, 2001:** Establish thermal stability of the SEI layer on graphite anodes in GEN 2 electrolyte. Identify some routes to improved stability *via* electrolyte additives and/or graphite pre-treatment.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONES:** Our major milestone to install and calibrate a new IR microscope is postponed to April 2001 due to the delay of equipment funds. Another new milestone is set to demonstrate that one of our diagnostic techniques can identify a failure mechanism in a Li-ion battery.

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:** The microscope is set up. A cell designed for *in situ* electrochemical experiment for the IR microscope is being built and is near completion. It was demonstrated that the rotating ring disk electrode (RRDE) is useful in detecting both reduction and oxidation species soluble in the electrolyte, which helps in identifying SEI layer formation mechanism.

The ring anodic current indicates that some soluble species from both EC and PC reduction diffuses to the ring and are re-oxidized at a ring potential of 3.5 V. In the case of EC, ring current increases approximately in a square root relationship with the rotating speed  $\omega$  (500, 1000, 2000 rpm), indicating a diffusion-limited process. The collection efficiency was calculated to be 6%. The reduction process of PC, however, is more than just a simple mass-transfer process. Therefore the collection efficiency on the ring could not be obtained. The rate of electron transfer seems to play a role as well. It is not clear from this experiment alone, however, whether it is reduction at the disk, re-oxidation on the ring or both, that are the rate-determination steps. Cyclic voltammetry (CV) results point out that at least the PC reduction process is kinetically slow. This is consistent with the general observation that PC is co-intercalated first with  $\text{Li}^+$  into graphite and subsequently reduced inside, causing exfoliation of the electrode.

Similar RRDE experiments were carried out for the oxidation of electrolyte EC/DMC- $\text{LiPF}_6$  (1:1) (Fig. 1A). Oxidation was observed to start at potentials above 5 V on the Pt disk (Fig. 1B), which is consistent with our computational results reported previously<sup>1</sup>. Gas production (possibly  $\text{CO}_2$ ) was observed. Computational studies are being carried out to investigate the products formed from both solvent oxidation and reduction. This would help the understanding of solvent reaction mechanisms as well as the gassing problems reported by SAFT.

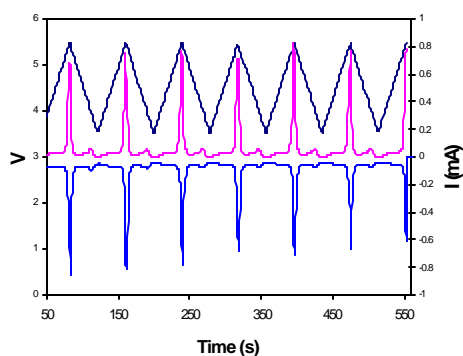


Figure 1A

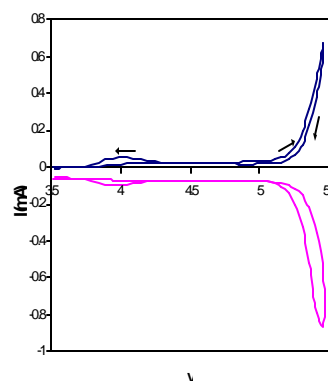


Figure 1B

- **Further plans to meet or exceed milestone:** None
- **Reason for changes from original milestone:** N/A

### Reference:

X. Zhang, J.K. Pugh and P.N. Ross, Jr., Computation of Thermodynamic Oxidation Potentials of Organic Solvents Using Density Functional Theory (DFT), *J. Electrochem. Soc.*, **148**, 183-188, (2001).

## TASK STATUS REPORT

**PI, INSTITUTION:** E.J. Cairns, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - Synthesis and Characterization of Electrodes

**SYSTEMS:** Li-Ion and Li-polymer Batteries

**BARRIER:** Rapid capacity fade

**OBJECTIVES:** The primary objectives are (1) to directly observe Li in BATT Program cathode materials, characterize the Li atomic and electronic local environment, and determine changes in this environment with cycling; and (2) to synthesize intermetallics that have higher capacities than carbon electrodes and that demonstrate stable capacities during cycling.

**APPROACH:** Our approach is to use  $^7\text{Li}$  MAS-NMR to characterize electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. We prepare intermetallics in the Mg-Sn system by mechanical alloying. Characterizations are performed with X-ray diffraction and microscopy techniques.

**STATUS, OCT. 1, 2000:** Milling conditions to synthesize cubic and rhombohedral forms of  $\text{Mg}_2\text{Sn}$  were determined. Amorphous Mg-Sn alloys could not be produced by mechanical alloying in a typical high-power ball-mill. Attempts to synthesize a metastable, cubic  $\text{Mg}_{5.67}\text{Sn}$  alloy were started. Cycling tests showed that cubic- $\text{Mg}_2\text{Sn}$  capacities can exceed capacities for carbon electrodes, but the capacities fade below 100 mAh/g after a few cycles. Comparisons between fine-grained  $\text{Mg}_2\text{Sn}$  and coarse-grained  $\text{Mg}_2\text{Sn}$  show that the microstructure of these intermetallics influences electrochemical performance. X-ray diffraction of cycled electrodes indicates that a major mechanism for the capacity decay is conversion of the intermetallic into Mg and Sn.

**STATUS SEPT. 30, 2001:** We expect to have compared  $^7\text{Li}$  MAS NMR spectra for stoichiometric and substituted tunnel-structure manganese oxides after electrochemical cycling. We expect that this information will elucidate the structural changes accompanying capacity fade. We expect to have completed NMR analysis of fresh  $\text{LiFePO}_4$ -based materials, and begun long-term cycling experiments on these materials. We will have concluded our evaluation of the Mg-Sn system. We plan to perform NMR experiments to aid in the characterization of the microstructure of the intermetallics and to determine sites that are occupied by lithium. We expect to have identified the role of the microstructure in  $\text{Mg}_2\text{Sn}$ , studied through experiments on as-milled samples and on annealed samples, on the electrode capacity and cycle life. Similar work will be performed on the metastable, rhombohedral- $\text{Mg}_2\text{Sn}$  phase to determine if this more conductive phase retains its structure during cycling.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONES:** Our major milestones are to compare NMR-observable properties of stoichiometric and substituted tunnel-structure electrodes before and after cycling, and to complete work on the cubic- $\text{Mg}_2\text{Sn}$  phase by April 2001.



## PROGRESS TOWARDS MILESTONES

- **Accomplishments toward milestone 1 during last quarter:**

$^7\text{Li}$  MAS NMR spectra for  $\text{Li}_x\text{Ti}_y\text{Mn}_{1-y}\text{O}_4$  and  $\text{Li}_x\text{Cu}_y\text{Mn}_{1-y}\text{O}_4$  have been obtained as described previously. Electrochemical cycling and modification of the Li content of these compositions is now under way. Spectra of  $\text{LiMPO}_4$  samples ( $\text{M} = \text{Fe, Mn, Co, Ni}$ ) have been obtained. A single isotropic line that displayed fast relaxation times characterized all spectra. An asymmetric spinning sideband manifold accompanies the isotropic line. The anisotropy in the magnetic interaction between unpaired electrons at the transition metal site and  $^7\text{Li}$  causes this asymmetry.  $\text{LiFePO}_4$  has been synthesized by several different routes. The NMR spectra of the resulting samples are nearly identical, indicating that the Li local environment is unaffected by synthesis conditions.

- **Further plans to meet or exceed milestone:**

- $^7\text{Li}$  NMR spectra of tunnel compounds will be compared before and after electrochemical cycling following the conclusion of cycling experiments, which are under way.
- Variable-temperature and -field NMR studies will be conducted on  $\text{LiFePO}_4$ -based samples to determine the shift and linebroadening mechanisms for these materials.
- $\text{Li(Fe,Mn)PO}_4$  samples, which are known to display a higher electrochemical potential, will be synthesized and evaluated with NMR at various states of charge, and after long-term cycling.

- **Reason for changes from original milestone:** N/A

- **Accomplishments toward milestone 2 during last quarter:**

Cycling rate and temperature effects on cycling performance of  $\text{Mg}_2\text{Si}$  have been evaluated. X-ray diffraction at various states of charge has been used to determine reaction mechanisms. Li insertion into  $\text{Mg}_2\text{Si}$  produces a Li-intercalated  $\text{Mg}_2\text{Si}$  phase that is converted to  $\text{Li}_2\text{MgSi}$  with further insertion. Li also reacts with Mg produced during formation of  $\text{Li}_2\text{MgSi}$ . The  $\text{Li}_2\text{MgSi}$  phase is converted to binary Li-Mg and Li-Si phases with additional Li insertion. Temperature and cycling-rate effects on maximum discharge capacities and capacity fade rates were determined.

- **Further plans to meet or exceed milestone:**

An *in situ* electrochemical cell for x-ray diffraction measurements has been built to reduce the time required to determine structural changes to electrodes during cycling.

- **Reason for changes from original milestone:**

The  $\text{Mg}_2\text{Si}$  system is more attractive than the  $\text{Mg}_2\text{Sn}$  system because of its higher specific capacity, so the focus of this part of the task has shifted to the former material. Otherwise, the objectives of the milestone remain unchanged.

## TASK STATUS REPORT

**PI, INSTITUTION:** J. Evans, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Diagnostics - EQCM Studies of the SEI on Carbon Anodes

**SYSTEMS:** High-power Li-ion battery

**BARRIER:** Irreversible capacity loss due to SEI formation and growth

**OBJECTIVES:** The primary objective is to understand SEI formation and growth on carbon anodes.

**APPROACH:** Our approach is to use an electrochemical quartz crystal microbalance (EQCM) to characterize the SEI formed on disordered carbon thin-film electrodes in model cells. Data to be collected are changes in mass of the SEI on the electrode and, thereby, the SEI growth with cell cycling is studied. A joint study to combine spectroscopic ellipsometry and EQCM gives us the SEI density.

**STATUS OCT. 1, 2000:** We estimated the SEI density on disordered carbon thin-film electrodes and observed mass changes corresponding to Li intercalation/deintercalation in 1M LiClO<sub>4</sub> / EC+DMC electrolyte.

**STATUS SEPT. 30, 2001:** We expect to correlate SEI formation and growth with the electrolyte LiPF<sub>6</sub> or LiTFSI/EC+DMC electrolyte and impurities (*e.g.*, H<sub>2</sub>O).

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONE:** Our major milestone to study the dynamic nature of the SEI as a function of electrolyte composition during cycling is expected to be completed by the planned date of July 2001.

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter:** The use of the EQCM to investigate the SEI layer has been complicated by an apparent, long term, mass increase (frequency decrease) of the electrode in some electrolytes. We have now identified this as being due to a hitherto undiscovered viscosity increase of the electrolytes. Not only does this have impact on the EQCM technique but it may be a significant mechanism of cell performance degradation; the conductivity of electrolytes generally decrease as their viscosities increase.

Viscosity of various liquids including 1 M  $\text{LiClO}_4/\text{EC}+\text{DMC}$  were measured throughout one day of storage in contact with carbon electrodes. Results are shown in Fig. 1 for various electrolytes. Three of the solutions experienced viscosity increases. All systems with viscosity increase contained EC+DMC. As the frequency decrease at OCV is common to all the electrodes used in this study (refer to the previous quarterlies), this viscosity change is also observed for three kinds of the electrodes (carbon, nickel, and aluminum). However, it is important to note that the three solutions of EC+DMC tested did not show viscosity change if they were stored in glass vials. For comparison, the viscosity change of 1 M  $\text{LiClO}_4 / \text{EC}+\text{DMC}$  electrolyte stored in a glass vial is inserted in Fig. 1.

To estimate the frequency change due to the viscosity increase, a theoretical equation that considers the viscosity effect on the resonant frequency was used. Although the agreement between measured and estimated frequencies is good for 1 M  $\text{LiClO}_4/\text{EC}+\text{DMC}$ , the estimated frequency changes in the other systems are too low by as much as 150 Hz in the case of PC. Nevertheless, it is evident that the viscosity change of electrolyte can account for the majority of the frequency decrease at OCV. Because the total measured frequency change is attributed to both viscosity changes of electrolyte and electrochemical/chemical reactions under consideration, the effect of viscosity on the resonant frequency should be quantified in interpreting the EQCM data.

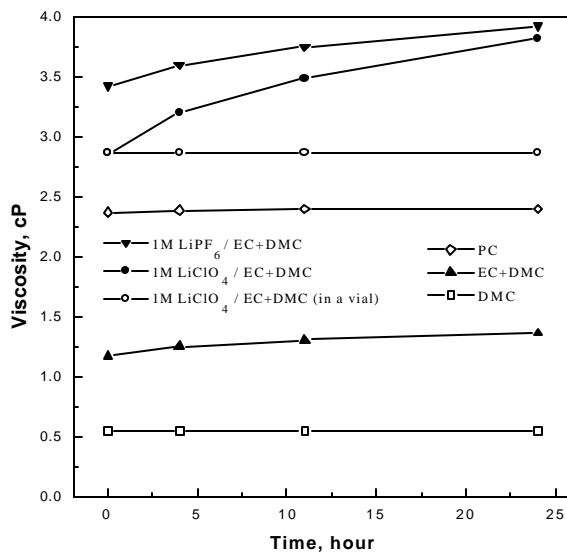


Figure 1. Viscosity change of various liquids with time.

- **Further plans to meet or exceed milestone:** None
- **Reason for changes from original milestone:** N/A

## BATT TASK 6 MODELING

### TASK STATUS REPORT

**PI, INSTITUTION:** J. Newman, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Modeling - Improved Electrochemical Models

**SYSTEMS:** Li/Polymer and Low-Cost Li-Ion

**BARRIERS:** Poor polymer transport properties, thermal management, dendrite formation

**OBJECTIVES:** Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

**APPROACH:** Use galvanostatic polarization technique to measure a complete set of transport properties, which aids selection of improved polymer electrolytes. Develop molecular dynamics program to predict diffusion coefficients in multicomponent solutions. Use potentiometric technique to measure entropy and develop thermal model that accounts for concentration effects in insertion electrodes, in order to improve thermal management. Develop model of factors affecting dendrite formation on Li metal. Use Raman spectroscopy to measure *in situ* concentration profile and dendrite growth.

**STATUS OCT. 1, 2000:** Measured transport properties in PEO-LiTFSI polymer electrolyte and improved the measurement technique. Completed computer program and simulations for electrolyte diffusion coefficient of NaCl and KCl in water. Used calorimetry to validate energy balance. Measured entropy in manganese oxides. Developed a preliminary model for dendrite growth which includes effects of surface tension. Developing Raman spectroscopy methods to examine dendrite growth *in situ*.

**STATUS SEPT. 30, 2001:** We expect to complete measurements of the transport properties of PEO-LiTFSI and to complete refinement of both the galvanostatic polarization method and the transition-time verification method. Modification of the molecular dynamics program to predict diffusion coefficients in multicomponent electrolytes currently of interest to the BATT program, such as LiBF<sub>4</sub> in EC:PC, will be ongoing. Measurements of the entropy of reaction in BATT baseline materials will be completed. Modeling of the SEI layer will be ongoing. Refinement of a model of dendrite growth to include relevant physical effects will be ongoing, as will experimental work to observe dendrite growth and concentration profiles *in situ* using confocal Raman spectroscopy.

**RELEVANT USABC GOALS:** Specific power 300 W/kg, 10 year life, <20% capacity fade.

**MILESTONES:**

1. Preliminary model of transport through the SEI layer by August 1, 2001.
2. Design a cell container for *in situ* confocal Raman microscopy by July 1, 2001.

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:** A continuum-scale numerical model is being developed for transport of Li ions and electrons through an SEI film, in order to understand how mechanisms of transport affect rates of side reactions. The model equations have been developed and programmed in finite difference form, meeting milestone 1. Work to refine the model is ongoing.
- **Accomplishments toward milestone 2 during last quarter:** (With Robert Kostecki)  
The measurements of transport properties (and growth of dendrites, see below) can be verified independently by using *in situ* confocal Raman spectroscopy. A cell design has been achieved that is of well-defined geometry, airtight, inert, transparent, and uniform temperature. Further improvements to meet milestone 2 are still needed to accommodate thermal expansion of cell materials.
- **Further plans to meet or exceed milestones:** None
- **Reason for changes from original milestones:** N/A

### Other Progress

Measurements of the transference number in LiTFSI-PEMO yielded negative values at low LiTFSI concentrations. Analysis of transition time experiments (with John Kerr) on PEMO-LiTFSI and PEMO-Li-triflate indicates the occurrence of an electrochemical side reaction at the Li electrode surface in PEMO-LiTFSI, particularly at low starting LiTFSI concentrations. We believe the side reaction involves the PEMO polymer, although impurities may also be involved. Transient simulations developed to assess the impact of such a side reaction on transport property measurements indicate that a side reaction can indeed affect the measurements and yield, for example, apparently negative transference numbers, primarily by altering the slope of the concentration-cell calibration curve.

The molecular dynamics code for predicting diffusion coefficients in multicomponent solutions has been changed to allow simulation of carbonate solvents. Preliminary simulations are in progress to refine intermolecular potential models for carbonate solvents and LiPF<sub>6</sub> salt.

We believe that the a major cause of the loss of capacity in Li-alloy negative electrodes is that the SEI layer grows in between alloy particles as they change volume during delithiation, causing loss of electrical contact. We have characterized the SEI layer on lithium-tin electrodes in propylene carbonate (PC) with 1 M LiClO<sub>4</sub> electrolyte. Analysis of the results was aided by comparing performance in PC to that in dioxolane. PC reduction begins above 0.8 V and consumes at least 60 mAh/g Sn of irreversible capacity. The interfacial impedance in PC is over three times larger than that in dioxolane. FTIR shows that the surface of the SEI layer formed in PC contains lithium-alkyl carbonates. Current-sensing AFM shows that the SEI layer in PC is completely insulating, and consists of a soft outer layer (alkyl carbonates) on top of a hard inner layer (inorganic salts). The shape and mixing of the conductive filler has a large effect on electrode capacity and rate of capacity fade. By mixing two shapes of conductive filler (flake graphite and acetylene black) in a blender, we achieved delithiation capacities of 230 mAh/g for over 24 cycles in our simple tin electrodes.

We have developed a model for dendrite growth and used it to evaluate the effects of various parameters on the dendrite growth rate. Analysis of interfacial forces has shown that the elastic properties of the separator control dendrite growth rate as much or more than surface forces during the early stages of growth. Therefore, we will examine, using stability analysis, whether there exists a parameter space of material properties under which growth of dendrites is suppressed by mechanical strain in the separator.

## TASK STATUS REPORT

**PI, INSTITUTION:** A.M. Sastry, University of Michigan

**TASK TITLE - PROJECT:** Modeling - Failure Mechanisms in Li-ion Systems: Design of Materials for High Conductivity and Resistance to Delamination

**SYSTEMS:** Low-Cost Li-Ion

**BARRIER:** Short lithium battery lifetimes

**OBJECTIVES:** The primary objective of these studies is to explain and predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

**APPROACH:** Correlation of delamination, high impedance and temperature/structure/function phenomena with specific materials composition and morphology will be developed, making use of the extensive software developed for tracking mechanical and conductive losses in heterogeneous materials at UM. Specific comparisons will be undertaken, using cells provided by the ATD and BATT programs.

**STATUS OCT. 1, 2000:** We developed finite element representations of model carbon materials, and developed a means for measuring conductivity of thin electrodes.

**STATUS SEPT. 30, 2001:** We expect to confirm structure/function relationships in ATD Gen 1 and Gen 2 cells, through image analysis and testing, with verification from finite element simulations.

**RELEVANT USABC GOALS:** 10-year life, <20% capacity fade over a 10-year period.

**MILESTONES:** We expect to test DOE ATD Program Gen 1 and 2 cells, provided by Argonne National Laboratories, by May 31, 2001 (start date: 2/01).

## PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have completed conductivity testing and initiated image analysis of materials from three laboratories participating in DOE-sponsored efforts: Argonne National Laboratory (Dr. Gary Henriksen, contact), Lawrence Berkeley National Laboratory (Dr. K. Kinoshita, contact), and the Institut de Recherche d'Hydro-Québec (Dr. Karim Zaghib, contact). Anode (LBNL, IREQ) and cathode (ANL) materials have been tested.

We have worked extensively in this period to understand large variations in experimental results using several techniques for conduction mapping. We have concentrated efforts on closed-form solutions of interacting conductive fields, in order to design more sensitive experiments. We have also continued to expand our simulations capability for multiphase materials. Our efforts can be summarized in this project period as follows:

1. experimental conductivity mapping of materials provided by three DOE-sponsored laboratories, has continued, using both two-probe and four-probe conduction experiments, with various tip geometries and spacings
2. mathematical design of experiments, to design improved conduction experiments
3. conductivity code development for automatic generation of irregular arrays of conductive particles with verification of recently added features to handle boundary effects and irregular particle connections
4. extension of mechanics modeling of more complex fiber interconnects, allowing 3D results to be used to implement revised mechanics assumptions in faster, more efficient 2D simulations, and also developing correlations between real material behavior and model behavior

- **Further plans to meet or exceed milestone**

We have requested more materials of LBNL for collaborative purposes. We have also continued work on materials supplied by IREQ. Our conduction and mechanics simulations have advanced in the project period, and we have also completed a set of calculations on improved design of conduction experiments.

- **Reason for changes from original milestone:** N/A

## **TASK STATUS REPORT**

**PI, INSTITUTION:** J. Evans, Lawrence Berkeley National Laboratory

**TASK TITLE - PROJECT:** Modeling - Thermal Modeling of Li Batteries

**SYSTEMS:** Li-polymer (Li-ion)

**BARRIER:** Thermal management and safety issues, battery efficiency

**OBJECTIVES:** The objective is the ability to predict the thermal behavior (including stability) and efficiency of Li batteries for use in electric or hybrid vehicles.

**APPROACH:** The approach is a combination of mathematical modeling and experimental measurement. The modeling couples the numerical solution of the equations for heat generation and transport within a battery to the equations describing battery electrochemistry. The experiments are to measure fundamental properties for input into the model or for comparison with model predictions. Thermal conductivities of cell components are measured, as are heat generation rates, in laboratory and commercial cells.

**STATUS OCT. 1, 2000:** A coupled mathematical model had been developed and found to show a reasonable fit to limited experimental data on heat generation during discharge of laboratory Li-polymer cells.

**STATUS SEPT. 30, 2001:** Limited progress made with the help of an undergraduate.

**RELEVANT USABC GOALS:** 75-80% discharge efficiency, thermal loss 15% of capacity in 48hrs, safety.

**RELEVANT USABC GOALS:** Tolerance to abusive operating conditions.

### **MILESTONES:**

December 2000 - examination of stability of Li-polymer cells for perturbations of long length scale.

April 2001 - restoring the electrochemical calorimeter to operating condition.

September 2001 - completion of measurements on Li-polymer cells available under the program.



## PROGRESS TOWARDS MILESTONES

### Accomplishments towards milestones over last quarter

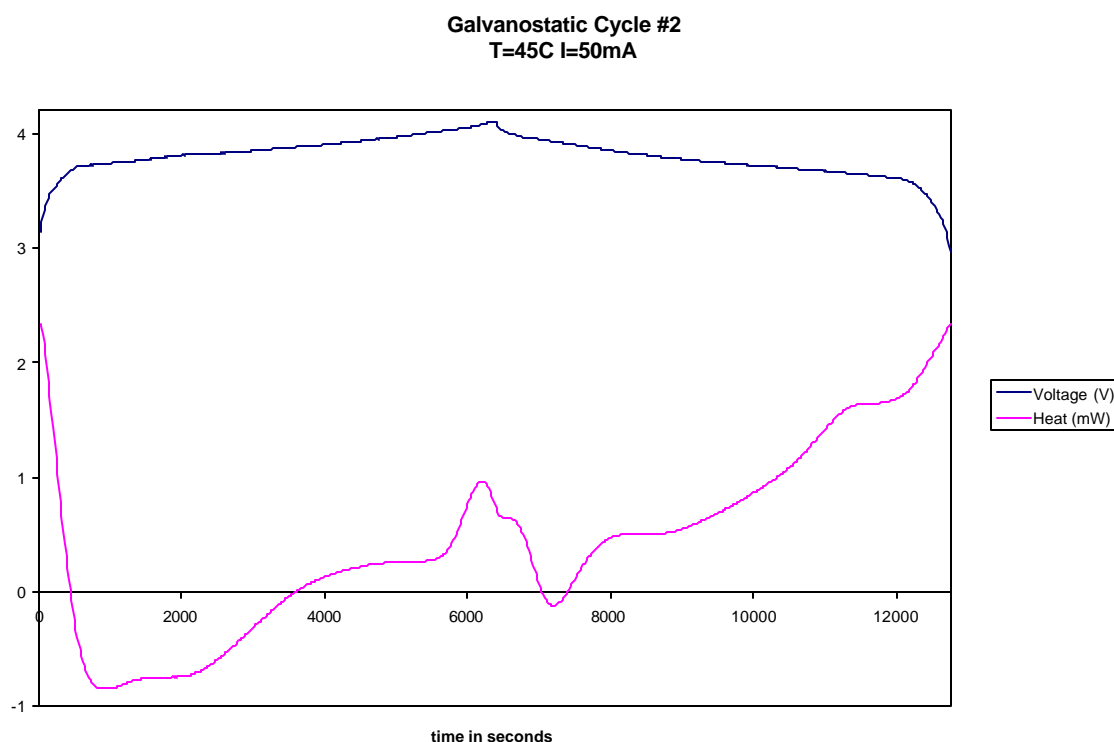
An undergraduate student was employed over the summer to conduct heat generation measurements in the electrochemical calorimeter. Heat generation rates have been measured on Li-ion cells (Li-cobalt oxide) obtained by LBNL at 30 and 45°C with currents of 25, 50 and 100mA. Fig. 1 is a typical result showing one charge followed by a discharge, both at constant current of 50mA. This plot is for the second cycle of the cell. The upper curve gives the cell voltage while the heat generation rate (negative is heat absorption) is given by the lower curve. Charged and discharged at this low rate, the cell is very efficient with heat generation being less than 1% of the electrical energy.

### Further plans to meet or exceed milestones:

Milestones completed to the best of our ability.

### Reasons for changes from original milestones:

Insufficient and uncertain funding. Unanticipated departure of graduate student.



## PROPOSALS UNDER REVIEW

<b>ORGANIZATION</b> <i>(Principal Investigator)</i>	<b>TITLE</b>	<b>STATUS</b>
University of Michigan <i>(A. Matzger/G.A. Nazri)</i>	Optimization of Li Ion Transport in Polymeric Electrolytes: A Theoretical and Experimental Approach	Request for Proposal - Under Review
Clemson University <i>(D. DesMarteau)</i>	New Battery Electrolytes Based on Oligomeric Lithium bis(perfluoroalkyl) imide Salts	Request for Proposal - Under Review
EIC Laboratories, Inc. <i>(G.L. Holleck)</i>	Applied Research on Novel Electrolytes for Advanced Rechargeable Lithium Batteries	Request for Proposal - Under Review
Pennsylvania State University <i>(H.R. Allcock)</i>	Optimization of SPE Battery Performance Through the Development of Novel Electrolytes and Cathodes	Request for Proposal - Under Review
University of Minnesota <i>(W.H. Smyrl/B.B. Owens)</i>	Novel Solid Polymer Electrolyte Systems	Request for Proposal - Under Review
University of South Carolina <i>(P.B. Balbuena)</i>	Modeling of Salt Chemistry in Li-Ion Battery Electrolytes	Request for Proposal - Under Review
University of Utah <i>(G.D. Smith)</i>	A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Li Cations in Polyether-Based SPEs	Request for Proposal - Under Review
Covalent Associates <i>(A.B. McEwen)</i>	Ionic Liquid Electrolyte Safety Determination and Optimization	Request for Proposal - Under Review
University of Michigan <i>(M.D. Curtis/G.A. Nazri)</i>	New Single-Ion Electrolytes for Li-Ion Battery Technology	Request for Proposal - Under Review

# **BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)**

## **QUARTERLY REPORT FOR APRIL – SEPTEMBER 2001**

### **CALENDAR OF UPCOMING EVENTS**

#### April 2001

- 2 - 5      Space Power Workshop – Redondo Beach, CA (Jackie Amazaki, 301-336-4073;  
[Jacqueline.y.amazaki@aero.org](mailto:Jacqueline.y.amazaki@aero.org); <http://www/aero.org/conferences/power>) Crowne Plaza
- 17 - 19     Batteries 2001 – Paris, France ([www.batteries2001.com](http://www.batteries2001.com))

#### May 2001

- 11 - 14     PES 2001, Polymer Electrolytes Symposium – The Netherlands (Symposium Secretariat:  
c/o LGCE, P.O. Box 83005, NL-1080 AA, Amsterdam, The Netherlands; +31 20 679  
3218; fax: +31 20 675 8236; [PES2001@lgce.nl](mailto:PES2001@lgce.nl))

#### July 2001

- 1 - 6        International Conference on Materials for Advanced Technologies – ICMAT 2001 –  
Singapore (B.V.R. Chowdari, Department of Physics, National University of Singapore, 10  
Kent Ridge Crescent, Singapore 119260; 65-874-2956; fax: 65-777-6126;  
[phychowd@nus.edu.sg](mailto:phychowd@nus.edu.sg); <http://www/mrs.org.sg/icmat2001>)
- 9 - 13       International Conference on Electrified Interfaces: 9<sup>th</sup> in a Series on Non-Traditional  
Methods – Nova Scotia (Dr. Sharon G. Roscoe, Chemistry Dept., Acadia University,  
Wolfville, Nova Scotia, Canada B0P 1X0; fax: 1 9025851114; [sharon.roscoe@acadiau.ca](mailto:sharon.roscoe@acadiau.ca))

#### September 2001

- 2 - 7        2001 ECS - Joint International Meeting of ISE and ECS– San Francisco CA (Dr. O.  
Dossenbach; [odossenbach@pingnet.ch](mailto:odossenbach@pingnet.ch))

#### December 2001

- 11 - 14     The EVAA Electric Transportation Industry Conference & Exposition 2001– Sacramento,  
CA (Registration Headquarters, 499 Seaport Court, Suite 300, Port of Redwood, CA  
94063; 800-260-8972, fax: 650-369-0618; [information@connectionsww.com](mailto:information@connectionsww.com);  
<http://www.evaa.org>)

#### May 2002

- 12 - 17     201st Electrochemical Society Meeting – Philadelphia, PA – ECS Centennial Meeting (The  
Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609)  
737-1902, fax: (609) 737-2743; [ecs@electrochem.org](mailto:ecs@electrochem.org))

### June 2002

- 23 – 28      11<sup>th</sup> International Conference on Lithium Batteries (IMLB-11) – Monterey CA (IMLB 11 Conference Secretariat, c/o The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/011/imlb11.html>)

### July 2002

- 14 – 19      EESAT 2002 - International Ceramics Congress - Materials for Electrochemical, Chemical, Nuclear and Environmental Applications – Florence Italy (Dr. Nancy Clark, Sandia National Laboratories, P.O. Box 5800, MS 0613, Albuquerque NM 87185; nhclark@sandia.gov; <http://www.dinamica.it/cimtec>)

### September 2002

- 3 - 8          53rd ISE – Dusseldorf, Germany (Prof. J.W. Schultze, Institut für Physikalische Chemie II, Universität Dusseldorf, Universitätsstr 1, D-4000 Dusseldorf 1, Germany; fax: 49 2118112803; schultzj@rz.uni-duesseldorf.de)

### October 2002

- 15 - 18      17<sup>th</sup> International Electric Vehicle Symposium & Exposition – Montreal, Canada (Ms. Pam Turner, EVS-17 Symposium Manager; (650) 365-2802; fax: (650) 365-2687; [electricevent17@aol.com](mailto:electricevent17@aol.com)).
- 6 - 11          202nd Electrochemical Society Meeting – Salt Lake City, UT (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org)

### August 2003

- 31 – Sept. 5      54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

### September 2004

- 55th ISE – Thessaloniki, Greece (Prof. E. Theodoridou)